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HOME ECONOMICS

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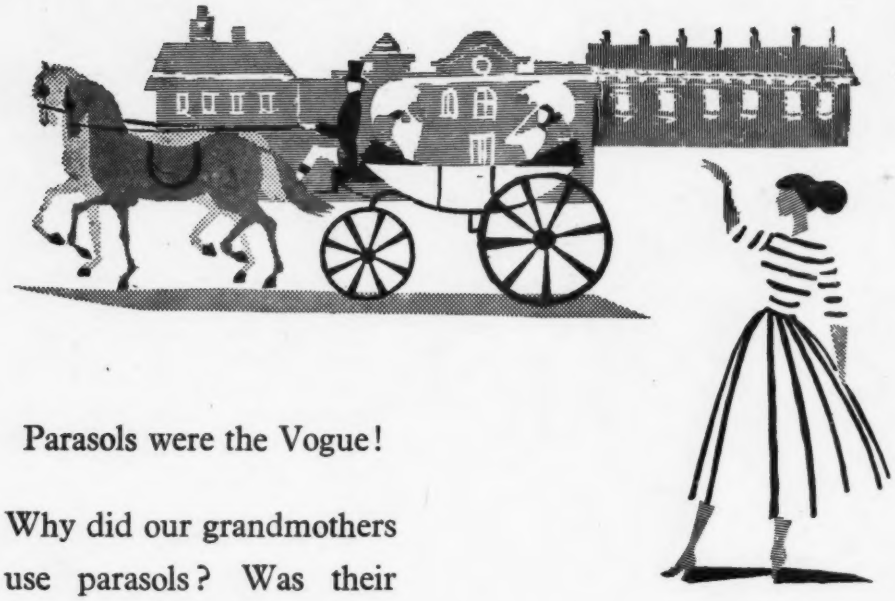

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Meeting held at the Great Northern Victoria Hotel, Bradford, on 8th December 1949, Mr. J. M. GOODALL in the chair

Recent Developments in Non-shrink Processes for Wool

P. ALEXANDER

THE SUBCUTICLE AND EPICUTICLE MEMBRANES

Besides the well known morphological components of the wool fibre, the scales and the cortical cells, there is clear evidence now of two membranes. Lehmann, Reumuth, and Zahn[1] recognised the so-called subcuticle membrane situated between scales and cortex some ten years ago by its greater resistance to chemical agents. Their methods of detection were not, however, completely unambiguous, and as a result their excellent work is not generally accepted[2]. We have found a simple method of isolation[3] of this membrane, which clearly establishes its existence, by the use of peracetic acid; this reagent rapidly oxidises the disulphide bond[4] in wool to two sulphonyl groups, without attacking any other major point in the wool molecule. When more than 90% of the cystine has been converted to cysteic acid, the wool becomes soluble in dilute ammonia, and the dissolved material behaves like a typical protein and is precipitated at pH below 5. Even after the most prolonged peracetic acid treatment, however, there remains a fraction, insoluble in ammonia, weighing approx. 7–10% of the original wool. The insoluble fraction is in the form of a continuous membrane running the whole length of the fibre, and from microscopic observation of the dissolution it appears to be situated between the scales and the cortical cells.

The membrane is a protein, and preliminary results suggest that it contains the same amino acids as the fibre as a whole but that they are not in the same proportions. The infra-red absorption spectrum (1–16 μ.) of the membrane is identical with that of the soluble wool obtained by precipitation from the ammonia solution. The cause of its greater chemical resistance is not known, and cannot be due to a high cystine content, as this amino acid is completely oxidised during the isolation of the membrane. It is possible that this membrane holds the scales in place, and that it may play an important part in the action of non-shrink reagents which lead to scale stripping.

The second membrane was discovered by Lindberg *et al.*[5] last year and is situated on the surface of the scales. It is very thin and represents less than 0·1% of the total wool substance. It is easily ruptured mechanically, and this may explain why it is non-continuous and covers only one or two scales in wool which has undergone ordinary processing. It is of non-protein composition and in all probability chemically similar to the fatty epicuticle of insects and leaves. The paradox of wool having a high regain and yet being hydrophobic may be due to this epicuticle, and wetting out probably proceeds by diffusion through the cracks of the membranes. In this way the easier wetting out of mechanically damaged wools and chlorinated wools receives an explanation.

Mercer, Lindberg, and Philip[2] have criticised earlier work on the subcuticle membrane, and have suggested that it consists of epicuticle with some scale substance adhering to it, as it is claimed that scale-like striations in it can be seen under the microscope. This criticism cannot be applied to the membrane as isolated by our method since— (*a*) no scale-like striations are visible; (*b*) repeated treatments with peracetic acid followed by ammonia do not reduce the quantity of insoluble protein, which must therefore represent a distinct fraction; and (*c*) treatment with chlorine does not collapse the membrane, although the epicuticle is removed by this treatment and this ought, according to Mercer *et al.*, to bring about disintegration.

FACTORS RESPONSIBLE FOR FELTING SHRINKAGE

The unique surface property of wool, the differential frictional effect (D.F.E.), by which the friction in the root-to-tip direction is less than in the tip-to-root direction, resides in the scale structure, and when this is removed the wool loses its tendency to felt[6]. Before felting can take place, however, the fibres must be capable of moving, and in a tightly woven fabric the fibres travel by the application of stresses which produce repeated extension and relaxation of the fibres.

Speakman[7] has shown that a measure of unshrinkability, especially in woven fabric, can be obtained by increasing the elastic modulus by cross-linking or by depositing resins in large quantities within the fibre. There is, however, no need to discuss processes based on this principle, since in every case so far described good unshrinkability is obtained only if the fibres are modified to such an extent that the treated material loses its wool-like character. The curliness[8] of the fibres is probably a contributory factor in felting similar to elasticity.

All commercially practicable anti-shrink processes function according to two mechanisms—

(1) Removing or decreasing the D.F.E. by raising the with-scale coefficients or lowering the anti-scale coefficients, and thus removing the fundamental cause of felting; this can be achieved by wholesale removal of scales, by partial degradation of the surface, or by masking the scales with polymers.

(2) Gluing together the fibres within a yarn and thus preventing fibre movement. Most resin processes function by this technique, and the binding

occurs locally and is well described by the term "spot welding" used by G. L. Royer.

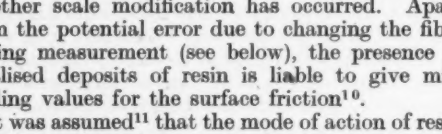
Any process which functions by the "spot welding" mechanism can readily be recognised from the fact that the wet tensile strength of yarns, particularly those of low twist, is increased without any change in the elasticity of the individual wool fibres[9]. Certain destructive processes, such as acid chlorination, give an increase in dry tensile strength of yarns under some conditions, because the degradation products formed act as a cement. This increase is not maintained if the measurements are made wet, and the strength of single fibres is almost invariably decreased.

Measurements of fibre friction to determine the D.F.E. do not give an unambiguous answer as to whether scale modification has occurred. Apart from the potential error due to changing the fibre during measurement (see below), the presence of localised deposits of resin is liable to give misleading values for the surface friction[10].

It was assumed[11] that the mode of action of resin processes where deposition occurs on the surface was by scale masking. Detailed investigation in this laboratory has shown that in the resin processes described only those using the silicones function in this manner, and in all the others the gluing together of fibres is the chief factor, with a reduction in D.F.E. as a subsidiary cause of shrinkage reduction.

THE ANHYDROCARBOXYGLYCINE PROCESS

Speakman and his coworkers[12] found that treatment of wool with anhydrocarboxyglycine in an organic solvent, under conditions where the latter can polymerise to form polyglycine, leads to almost complete unshrinkability with a resin deposit of 4% on the weight of the wool—



The process was believed to act by scale masking coupled with an adhesive effect, and the importance of the latter for the production of unshrinkability was first recognised by Speakman[12]. Alexander, Bailey, and Carter[13] demonstrated that the reduction in D.F.E. of treated fibres is small and that different methods of measurement give different values, but in no case is the D.F.E. reduced by more than 40%. A reduction of this magnitude, achieved for example by chlorination, would result in a small reduction in shrinkage only, in no way comparable with that obtained with anhydrocarboxyglycine. That "spot welding" is the major factor in the non-felting is indicated by the increase in tensile strength of treated yarns of approx. 50%, and further supported by the photomicrographs (Fig. 1) representing a typical sample of an anhydrocarboxyglycine-treated pattern.

We found[13] that wool of pH below 5 could not be rendered unshrinkable with anhydrocarboxyglycine, and that conditioning wool to a pH of about 9 leads to much more effective treatment. The water in the wool catalyses the condensation of anhydrocarboxyglycine to polyglycine, and the pH was shown to have a powerful effect on the size of the polymer produced. The average molecular weight at pH 5 was approx. 500, whereas at pH 9 it was greater than 2000.

Speakman thought it probable that the polymer is chemically linked to the wool via amino groups and that the effectiveness of the process is due to this anchoring, which prevents the polymer from coming off the wool. The theory is based on two series of experiments. The first claimed to show that the polymer cannot be removed from the wool by extraction with a solution of 50 g. of lithium bromide in 100 c.c. of water, which dissolved a sample of the polymer obtained by adding water to a solution of anhydrocarboxyglycine. The second claimed that deaminated wool cannot be rendered unshrinkable with anhydrocarboxyglycine.

We found, contrary to these experiments, that the polymer can be removed from wool, and the felting properties of the latter restored, by extraction with a solution of 100 g. of lithium bromide in 100 c.c. of water. The solubility of the polymer in lithium bromide solution decreases with increasing molecular weight. A sample of low molecular weight dissolved in a 50% solution, whereas a 100% solution was necessary for a sample of high molecular weight. The molecular weight depends on the purity of the anhydrocarboxyglycine and its method of preparation, and we found that the molecular weights obtained if the polymerisation takes place by slow release of water from the wool were quite different from those obtained by addition of water to a solution of anhydrocarboxyglycine.

In our hands, also, deaminated wool was readily rendered unshrinkable with anhydrocarboxyglycine once it had its excess acidity removed and was adjusted to pH 5. The experiments on the influence of the pH of the wool offer an obvious explanation of Speakman's results, since after deamination the wool is in an acid condition, which is difficult to remove without an alkaline aftertreatment. It was this acidity and not removal of amino groups which was responsible for the lack of shrinkage resistance.

The polymer is therefore held to the fibre by physical forces and hydrogen bonding only. Short polypeptide chains like those in the polymers of low molecular weight produced under acid conditions would not have the same scope for hydrogen bonding as the larger molecules, and this would explain their failure to prevent felting.

Since anhydrocarboxyglycine is very sensitive to moisture, which makes its handling difficult, a large number of related compounds of greater stability based on other amino acids and on sulphur-substituted amino acids were examined. With the exception of the DL-alanine derivatives, which gave some shrinkage resistance, none of the others gave polymers which prevented felting. The polypeptides formed can probably not form a firm union with the wool via hydrogen bonds, because the molecular weights in most cases are small, and also because the introduction of bulky side groups prevents close alignment with the wool molecules.

The anhydrocarboxyglycine process, however, gives very good results, especially if the wool is

uniformly adjusted to a slightly alkaline pH, which results in even deposition of polymer. The handle of wool treated without careful pH equalisation tends to be harsh, but this is prevented by pre-treatment in a buffer, which at the same time enables complete unshrinkability to be obtained with a smaller resin deposit.

APPLICATION OF MELAMINE–FORMALDEHYDE RESINS

Several firms have brought out non-shrink processes based on melamine–formaldehyde resins. Their behaviour is in many ways similar to urea–formaldehyde resins, and the usual procedure was to pad unpolymerised methylolmelamine, a condensate of melamine and formaldehyde, on to the wool and to condense it to an insoluble resin by baking above 110°C. in the presence of an acid catalyst[14]. Since cross-sections of the treated fibres took up no stain[15], it was concluded by the early workers that the resin was within the fibre. Further work showed, however, that the deposit was entirely on the surface, and that the fibre was not stained with the dye used because of the cross-linking action of excess formaldehyde which is always present in the monomer, and similar results can be obtained with formaldehyde at high temperatures alone. This resin treatment works almost entirely by the "spot welding" principle, the tensile strength of the yarn being greatly increased and the D.F.E. remaining unaffected[9].

Although good unshrinkability can be obtained, the melamine process had not received wide acceptance because the handle was harsh and there was no suitable baking equipment available for wool finishing. The process has now been modified[16] by partly precondensing the resin and applying it as a colloid which becomes fully cross-linked at temperatures below 100°C., which can be attained during ordinary drying. Furthermore, by first modifying the surface of the wool with hydrogen peroxide, unshrinkability can be obtained with a very much smaller quantity of resin, and this results in a better handle. This new process[17,18] has been shown to function by both scale masking due to a uniform film over the fibre and by "spot welding". It is not yet known which of the two factors is the most important in producing unshrinkability.

APPLICATION OF UREA–FORMALDEHYDE RESINS[19]

We found that the application of methylolurea followed by baking at 110–140°C. in the presence of an acid catalyst does not render wool unshrinkable unless more than 20% of resin is applied, which completely spoils the handle. The resin thus applied is not firmly fixed but comes off on washing. A wash-fast deposit giving good unshrinkability is obtained if the monomer, after padding on to the wool, is heated to 110–130°C. in the absence of an acid catalyst and then polymerised by baking with a catalyst. During the first cure no polymerisation takes place, and it seems possible that some of the monomer combines with the wool during this process. There is no doubt that the process functions by binding the fibres and preventing free movement (see Fig. 2).

VINYL POLYMERS

Unshrinkability by "spot welding" can also be obtained with vinyl polymers. The Montclair Research Corporation found that copolymers of butadiene and methyl methacrylate, within a narrow range of compositions, are capable of producing excellent unshrinkability with small deposits and without loss of handle[20]. Polymers from either of the two monomers alone or copolymers of the wrong composition do not produce unshrinkability. It is clear that the physical properties of the polymer play a vital part in obtaining a satisfactory finish, and that it must be neither too hard and brittle (i.e. contain excess methyl methacrylate) nor too rubbery (i.e. contain excess butadiene).

This process has not achieved industrial success because the polymer is highly inflammable, and also because it deteriorates on long storage, so that treated wool becomes tacky after one to two years.

We showed[21,22] that polymethyl methacrylate and polystyrene can render wool unshrinkable if the correct quantity of plasticiser is present, but its concentration is critical (as may be seen from Table I), whereas no satisfactory results were obtained with polymers from vinyl chloride, vinyl acetate, or acrylonitrile (vinyl cyanide).

The best method of depositing these resins is to apply them as an emulsion formed with an anionic agent, using wool which has been pretreated with a cationic agent such as cetyltrimethylammonium bromide or cetylpyridinium bromide. The negatively charged emulsion is attracted on to the

TABLE I

Permanence of Deposit and Shrinkproofing Properties of Methyl Methacrylate Polymers of Varying Plasticiser Content[21]

(Shrinkage of control 35·0%)

Diethyl Phthalate in Resin (% by wt.)	Weight Increase of Wool (%)— Immediately after Treatment	After Single Laundering	After Repeated Laundering	Shrinkage of Wool (%)
0	14·2	8·0	< 1	31·8
12	34·0	26·5	24·8	15·7
18	30·0	22·8	22·2	9·9
24	27·8	22·2	21·6	7·5
30	32·7	24·6	24·0	5·4
39	26·8	23·7	23·1	10·8
50	21·0	16·2	12·5	15·3
60	22·6	17·4	12·1	23·6
67	18·5	10·7	6·1	28·0

positively charged wool, and application can thus be made from a dilute bath, which is fully exhausted. This technique has great practical advantages over a padding procedure, besides giving a more wash-fast and therefore better anti-shrink finish.

The process can be used in two ways — either the monomer can be emulsion-polymerised with the plasticiser, and then applied as a resin emulsion to the wool[21]; or the monomer and plasticiser can be emulsified, exhausted on to the wool by the anionic–cationic technique, and polymerised *in situ* by adding a catalyst such as hydrogen peroxide to the bath[22]. Both methods give equally satisfactory results. In every case unshrinkability is obtained by binding fibres together locally, and there is no scale masking.

PROPERTIES NECESSARY FOR A "SPOT WELDING" RESIN

There are broadly two ways in which materials can be glued together— film adhesion and bridge

adhesion. The former is suitable for smooth surfaces, and uses a thin film of adhesive to even out submicroscopic roughness in order to ensure close contact between the surfaces, which is of itself sufficient to produce sticking. For wool fibres, bridge adhesion is required, and the function of the resin here is to make firm contact with the rough surfaces and to hold them together by forming a bridge. The bridging material must be neither too rubberlike nor too brittle, and this undoubtedly explains the critical composition required of vinyl polymers for shrinkproofing. The mechanical properties of a polyglycine of low molecular weight are quite different from those of the samples of higher molecular weight, as can be seen from the fact that only the latter can be cast into films, and this difference is probably important for bridge adhesion. The resin, besides giving a mechanically sound bridge, must also form a link with the fibre, and the intermediate cure required in applying urea–formaldehyde resins is probably connected with the bonding of the resins to the fibre, since the polymers produced by the conventional and the two-cure methods are very similar.

SILICONE RESINS

Silicones are the only resins which prevent felting by scale masking only, without forming any fibre–fibre bonds (see Fig. 3). Our findings have already been published[23], so that only the main conclusions will be presented here.

Unshrinkability was obtained with 3–5% of resin if applied under conditions where it could chemically combine with the wool. It is possible to obtain the same polymer from different monomers of varying reactivities, but only those capable of reacting chemically with the wool gave a deposit which was wash-fast and produced unshrinkability. Extraction experiments with solvents capable of dissolving the polymer gave further unambiguous evidence of chemical combination with the wool under conditions where the treatment was effective. The –Si·NH– bond formed between wool and the silicones is easily hydrolysed, and after washing the resin is no longer anchored and can then be extracted. It appears that chemical bonding is necessary to obtain a uniform film-like deposit, but that once it is formed the wool remains unshrinkable if the links are broken.

It is possible, within the silicone group, to obtain a range of polymers varying from oils to brittle solids from different monomers, which, however, are all of similar reactivity and which all give chemically anchored polymers. It was shown that only a rigid solid is capable of masking the scales effectively, and oils, waxes, and rubbers failed to produce unshrinkability. Hard brittle polymers gave good results, and the requirements for scale masking are obviously different from those in "spot welding", where brittle polymers fail to function.

MODIFICATION OF THE SURFACE BY CHEMICAL ATTACK

Any reagent which removes the scales, or so loosens them that they come off during milling, renders wool completely unshrinkable[24]. Many of the common reagents used fall into this class, such as chlorine at pH below 8·5, chlorosulphamic acid[25], sulphuryl chloride[26], and ozone[27] (see Fig. 4 and 5). These processes, unless very carefully controlled, will result in loss of wool substance and give a product of poor wearing properties, since much of the resistance to abrasion of a wool is also impaired, and sometimes a harsh and at other times a slimy feel is produced. We have not been able to correlate feel with the nature of the damage. There is, unfortunately, no information available which enables handle to be identified by measurable properties of the fibres.

Another group of reagents, such as permanganate at pH below 2[28], hypochlorite at pH above 8·5 (the changeover in mechanism occurs within half a pH unit), fluorine[29], chlorourea at pH below 2[25], alkali dissolved in an organic solvent[30], and a mixture of hypochlorite and permanganate at pH 8·5–10 (Stevenson–Wolsey process)[31], leave the scales apparently unchanged and yet produce unshrinkable wool (see Fig. 6).

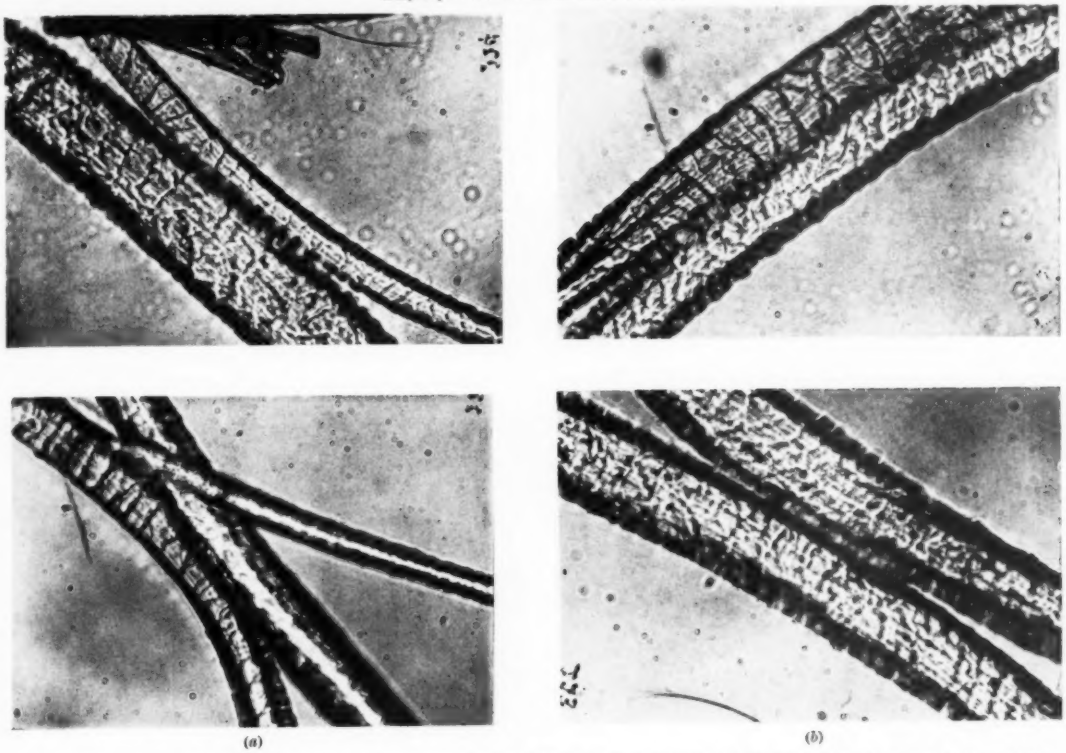
With the exception of the last two processes, however, all these reagents give partial unshrinkability only. Thus, wool treated with permanganate, for example, will not felt in a washing machine with soap however long the test is continued. It will felt, however, in the washing machine if the pH of the liquor is below 7, and in general the rate of felting will be almost as great as that of an untreated sample. Moreover, even in soap (i.e. at a high pH) the wool will felt if subjected to a milling action, in which the wool is mechanically compressed, whereas in a washing machine it only floats in the solution and no pounding of the fibres takes place.

A mixture of hypochlorite and permanganate at pH 8·5–10 and an alcoholic caustic soda process carried out exactly as in the patent[30] are the only treatments which do not remove the scales while still producing complete unshrinkability (i.e. resistance to acid washing and to milling). These facts can be explained on the basis of Rudall's theory[32] that the tips of the scales are responsible for producing the D.F.E. and that masking of the tips or their removal will lead to unshrinkability. Reagents which remove the scales naturally remove the tips as well, and the treated wool can thus no longer felt.

It may be suggested that treatments of the acid permanganate type only attack and soften without removing the scale tips. The softened scale substance acts as an adhesive and sticks to the next scale, thereby masking the tips. This scale is broken during the milling action, which bends the fibre, resulting in the forcing apart of scales and the liberation of the tip, and the capacity to felt is restored. Also the degraded protein which seals the scales together becomes hard and brittle in acid solutions and can then no longer act as an adhesive, so that the scales will become separated again and enable felting to take place in acid solution. The reagents which give complete unshrinkability without scale stripping must be assumed to have removed the tip completely, so that it cannot be restored by mechanical action with or without acid.

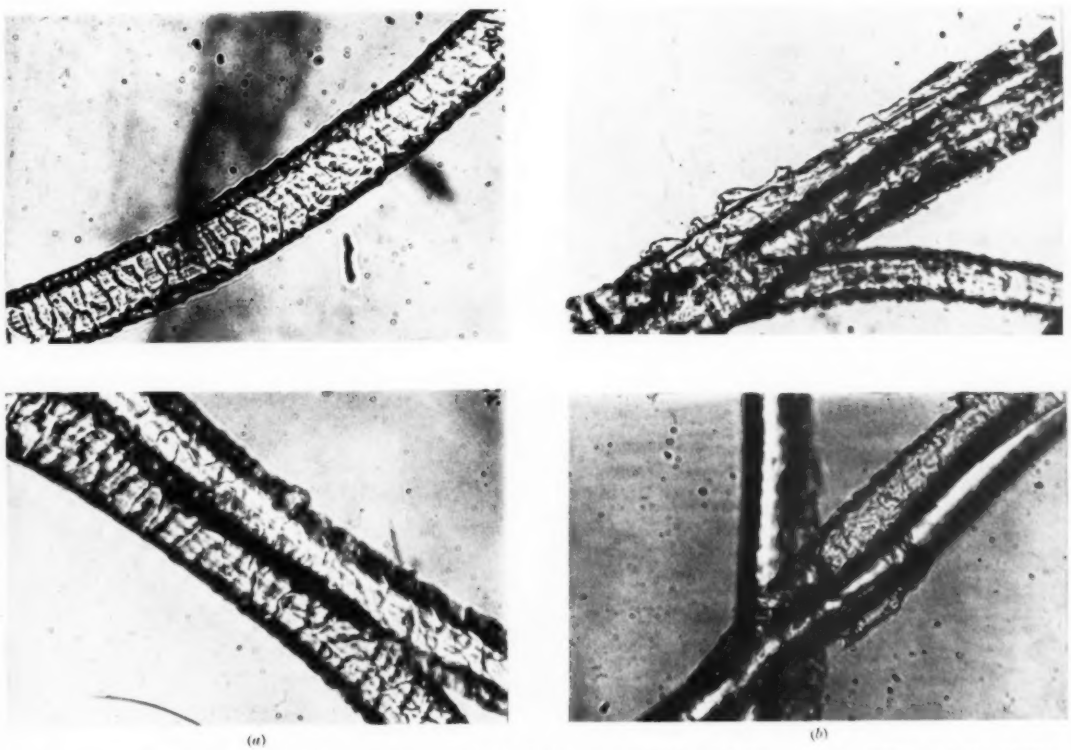
Photomicrographs (× 400) of Fibres

(All photomicrographs reproduced have been chosen after careful microscopic examination of several hundred fibres to ensure that they are truly representative of the treated fabric)



(*a*) (*b*)

FIG. 1— Fibres from a Fabric treated with Anhydrocarboxyglycine[11,12] showing "Spot Welding" of Fibres (*a*) before Milling, and (*b*) persisting after Milling in Soap



(*a*) (*b*)

FIG. 2 — Fibres from a Fabric treated with Urea–Formaldehyde Resin[19] showing "Spot Welding" of Fibres (*a*) before Milling, and (*b*) persisting after Milling in Soap

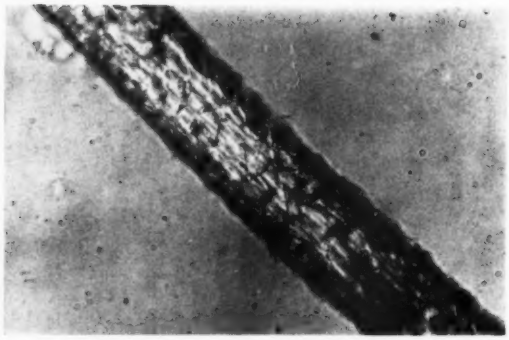
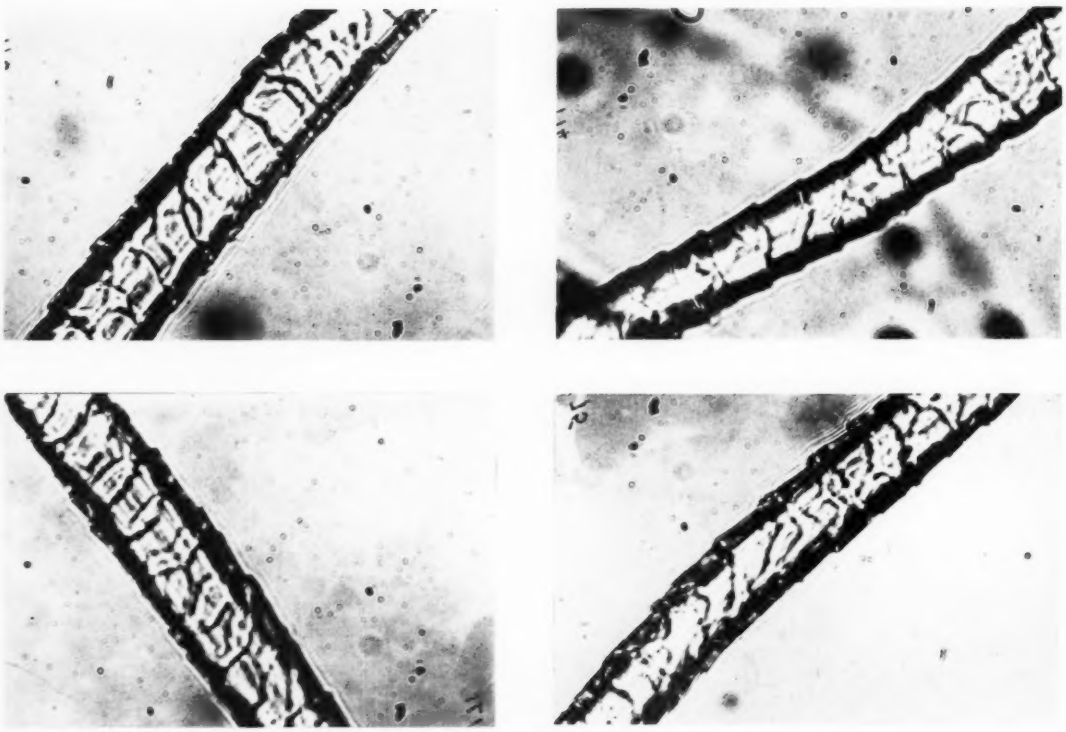
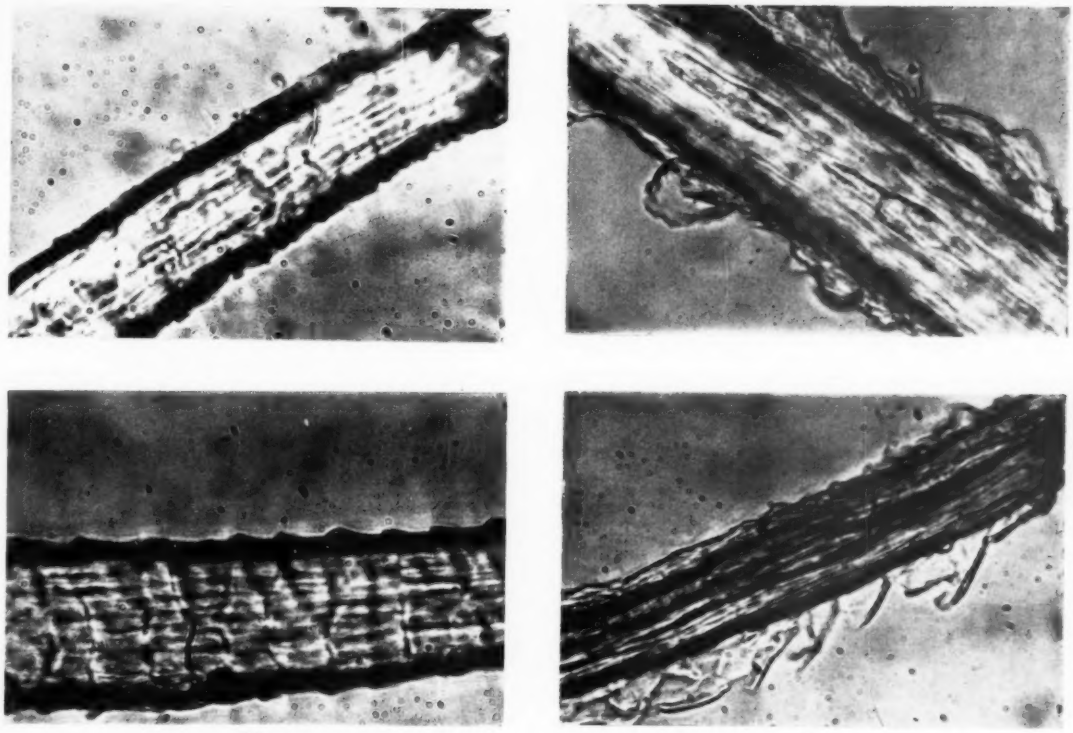


FIG. 3— Fibres from a Fabric treated with Methylsilicon Trichloride[23] showing Fibre Surface masked with Resin which is not removed by Milling in Soap. No case of "Spot Welding" could be found



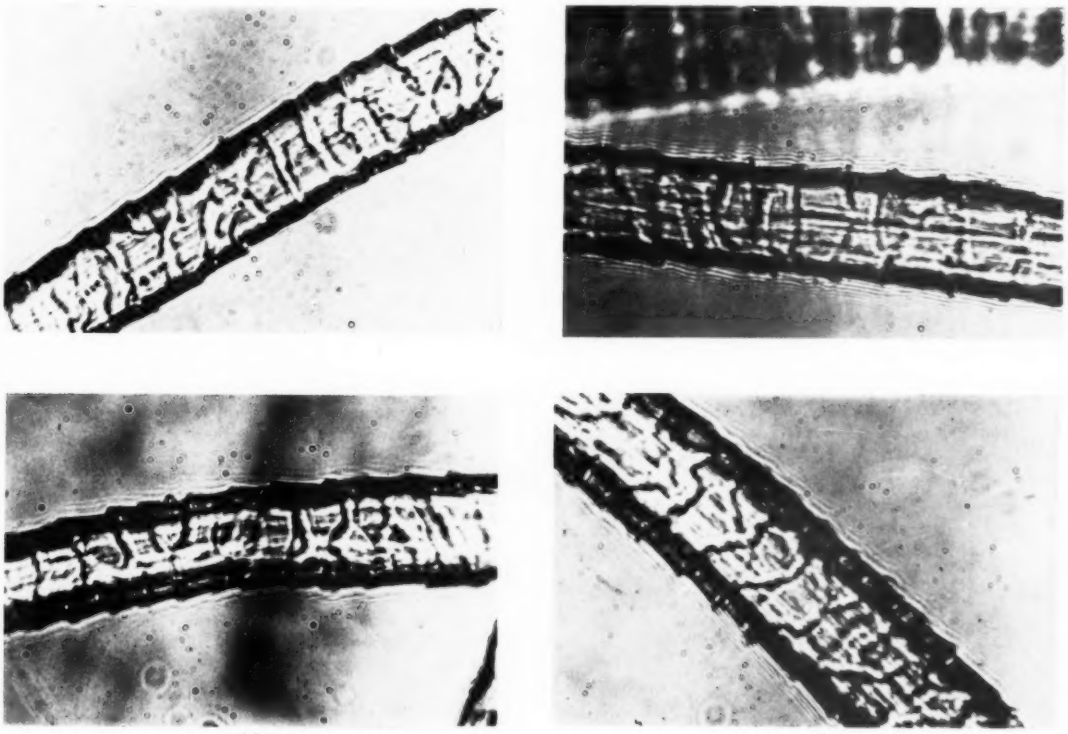
(*a*) (*b*)

FIG. 4— Untreated Fibres showing Scale Edges clearly (*a*) before Milling, and (*b*) after Milling in Soap



(*a*) (*b*)

FIG. 5— Fibres treated with Chlorosulphamic Acid[25] showing Scales (*a*) present after Treatment, and (*b*) becoming detached during Milling



(*a*) (*b*)

FIG. 6— Fibres treated with Chlorine and Permanganate at a pH about 9[31] showing apparently Unaltered Scale Structure both (*a*) before Milling, and (*b*) after Milling

Measurement of fibre friction also lends some support to the suggestion that the join produced by degraded protein can be broken by bending. Acid-permanganate-treated fibres show almost no D.F.E. from measurements by the "violin bow" technique[33], but when the frictional properties of these fibres are measured by the Lipson technique[34] then much of the D.F.E. is retained (Table II). In the former method the fibres are kept straight and no opening of the scales occurs, but in the other method the fibres are bent; this breaks the seal, frees the scale tips, and restores the D.F.E.

TABLE II

Corelation between Different D.F.E. Measurements

Treatment	Shrinkage (%)		D.F.E.	
	Washing Machine	Milling Stocks	Violin Bow Method[33]	Lipson Method[34]
None	24·0	25·1	31·0	0·23
4% Cl_2 at pH 2 ...	1·1	1·8	1·0	0·06
0·5% $KMnO_4$ at pH 2—				
10 sec.	0·0	18·1	1·8	0·17
30 sec.	1·0	7·6	2·4	0·05

We were at a loss to explain why wool which showed no D.F.E. as measured by the useful "violin bow" method still felted rapidly on milling. Since several treatments produced this effect we had become sceptical of the importance of the D.F.E. in felting[24,28], but the picture presented here seems to resolve this anomaly in a satisfactory way. It must be stressed that this hypothesis is purely tentative, and is put forward merely as a model on which to base further research.

At this point acknowledgment must be made to the help received from discussions with chemists at the American Cyanamid Co., notably Dr. G. L. Royer and Mr. H. E. Millson. The wonderful photomicrographs which they have obtained[35] support the scale tip ideas.

FACTORS INFLUENCING THE RATE OF THE REACTION

Having dealt with the chemical aspect of non-shrink reactions, we may now deal with the rate at which these reactions proceed and with the factors which will promote levelness.

A detailed treatment of the kinetics of the reaction between fibres and reactants in solution has been developed by us [36–38], on the basis of which the rate of reaction with chlorine and other non-shrink reagents can be satisfactorily explained. The problem is much more complex than indicated below, but the general picture presented will be essentially correct.

Any reaction between a liquid and a solid involves a number of steps, the slowest of which controls the overall rate of the process. In the case of the oxidation of wool, as also with dyeing, we know that the actual rate of reaction is very fast and that the slowest step is the transport of reagent to the site of reaction. There are two distinct steps involved, diffusion through the liquid and diffusion through the solid. Next to a solid immersed in a liquid there is an unstirred film of liquid, the viscous drag layer, in which the concentration of reactant varies from the concentration next to the solid surface to the uniform concentration of the bulk of the solution (Fig. 7). The process of, say, a chlorination is then the following— the reagent

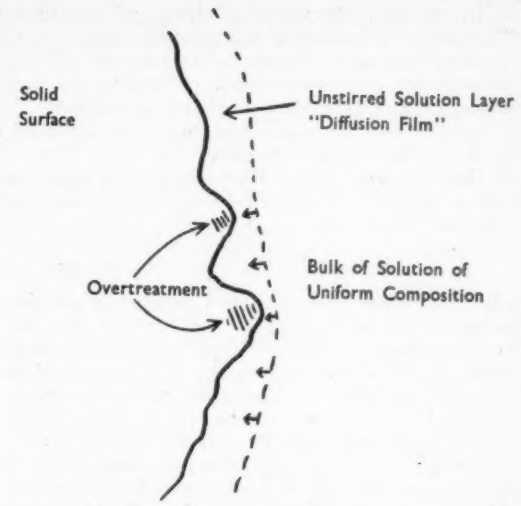


FIG. 7— Schematic Representation of Reaction of a Substance in Solution with a Solid such as Wool

diffuses from the bulk of the liquid through the liquid film, and then diffuses into the solid, where it is consumed. Now if the reagent is used up by the wool as quickly as it diffuses through the liquid film, then the rate of the reaction is controlled by this latter process. If, on the other hand, diffusion through the liquid film is rapid compared with diffusion in the solid, chlorine accumulates at the surface, which soon becomes saturated, and the rate is controlled by diffuson through the solid. It is clear that the treatment is most likely to be even under these conditions, since the rate, and therefore the extent, of the reaction at any one point becomes independent of all external influences such as fabric construction and uneven agitation. It is impossible that a liquid film next to, say, a knitted fabric will be of even thickness, since there is a streamlining effect over obstacles, and the shaded areas in Fig. 7 will be overtreated when the reaction is controlled by solution diffusion. The rate when controlled by fibre diffusion depends merely on the fibres themselves, which, though far from uniform in the case of wool, are randomly distributed, and unevenness over large areas of fabric is thus impossible.

Slow reaction in itself is no guarantee of even processing. If the transport of material to the fibre is very fast, even processing may still result, even though the overall rate is great. The real criterion is that the reaction should be controlled by fibre diffusion, which can be obtained in a given reaction by increasing the rate of diffusion through the liquid or by decreasing the rate of diffusion through the solid. The former can best be obtained by decreasing the thickness of the viscous drag layer by increasing agitation, although increasing the concentration of reactant and lowering the temperature will produce changes in the relative rates of the two processes which will favour control by fibre diffusion. The relative rate of solid diffusion can be influenced either by changing the surface area, being least with the thickest fibres, though this is clearly beyond the control of the processor,

or by changing the electrical charge of the fibres. The effect of agitation and pH of reagent (i.e. electrical charge of fibres) on the rate of aqueous chlorination will be discussed. Temperature and concentration have been discussed elsewhere[39].

AGITATION—The amount of reagent transported to the surface varies inversely with the thickness of the unstirred layer. The relationship between rate of agitation r and thickness of film d can be expressed as—

$$d \propto \left(\frac{1}{r}\right)^n$$

where n ranges from 0·5 to 1 depending on the nature of the solid surface[40]. We found that for knitted fabric $n=1$ over large ranges of stirring rates, so that there is a simple inverse relationship between the two[37]. Therefore, as we increase agitation more reagent reaches the surface, which will, at a particular stirring rate, become saturated. At this point the reaction becomes independent of stirring, as the rate will be controlled solely by diffusion into the solid (Fig. 8). In some reactions,

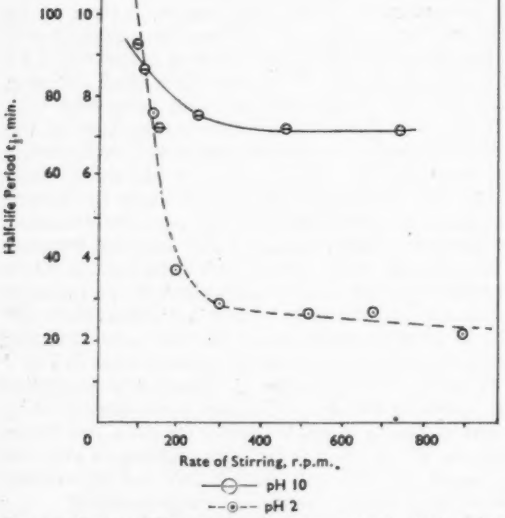


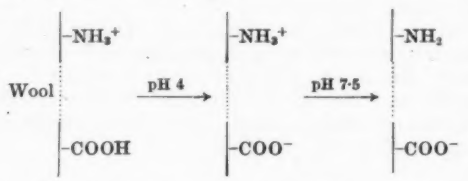
FIG. 8—Change of Rate of Reaction (represented by time of half exhaustion $t_{\frac{1}{2}}$) between Wool and Chlorine in Solution at pH 2 and pH 10 with Different Rates of Rotating the Fabric
Temp. 0°C.
Liquor : wool ratio 140 : 1
10% Chlorine on weight of wool

such as acid chlorination (pH 2) from dilute solutions at room temperature, the rate of removal of reagent from the surface is so great that to obtain agitation fast enough to give a sufficiently thin unstirred layer for surface saturation is very difficult in the laboratory, and certainly impossible under factory conditions. However, at a higher pH the removal from the surface becomes much slower for reasons which will be discussed later, and at quite a definite degree of agitation the rate becomes constant (see Fig. 8).

At this point it is apposite to consider different methods of agitation. In the experiments used for the graphs shown, the fabric was fixed to the stirrer, and thus the wool was moved relative to the liquid. It was found that rotating the fabric at 50 r.p.m. is equivalent to stirring the solution with an efficient propeller at 500–700 r.p.m. Wherever possible, therefore, anti-shrink processes should be carried out in machinery in which the wool is moved, and it is to be hoped that machine designers will study these problems and try to produce machines providing uniform agitation which results in the thinnest possible unstirred film.

ELECTRICAL CHARGE ON THE FIBRE—Up till now we have considered only means of increasing the relative rate of supply of reagent to the surface, but control by fibre diffusion can be promoted also by slowing down the rate of removal of reagent from the surface. If we slow down solid diffusion a smaller rate of transport through the liquid is necessary to keep the surface saturated, and the reaction can be carried out under fibre control conditions with less agitation, at lower concentrations, or at higher temperatures.

Owing to the amino and carboxyl groups the fibre assumes a positive charge at low pH values and a negative charge at high pH values. At intermediate pH values ranging from approximately 4 to 7·5 the fibre is uncharged, since the positive charges on the amino groups compensate the negative charges of the carboxyls, and the position may be formulated thus—



At pH below 4 the carboxyl group becomes uncharged and the fibre positive. At pH above 7·5 the amino group becomes uncharged and the fibre negative.

On the alkaline side diffusion of a positively charged ion will be promoted, whereas that of a negatively charged ion will be hindered by repulsion. The oxidising reagent in a solution of chlorine consists[4] at pH below 4 of Cl_2, and at pH 4–7 of HOCl, both uncharged molecules of similar size, neither of which would be repelled or attracted by

TABLE III
Effect of pH of Chlorination on Shrinkage of Wool

	Treatment pH	Shrinkage (%) Milling Stocks	Shrinkage (%) Washing Machine
No treatment	...	45·0	32·0
3% CHLORINE	5·2	1·1	1·0
	5·9	1·8	0·0
	6·8	0·0	0·0
	7·7	1·1	0·0
	8·1	11·0	1·2
	8·5	32·0	1·0
	8·9	43·0	5·9
	9·4	43·0	16·5
	10·1	43·0	18·0
3% CHLORINE	8·4	2·4	—
+	8·6	3·5	—
1·5% POTASSIUM	9·0	3·8	—
PERMANGANATE	9·5	8·0	—
	10·0	24·0	—

electrical charges on the wool, whereas at pH above 7 the solution contains more and more OCl^- ions. The latter will be repelled by the wool, which assumes an increasingly negative charge as the solution becomes more alkaline. In agreement with this picture, it is found that the rate of chlorination changes only slowly with pH below a value of 7, whereas at pH above 7 the rate decreases rapidly with increasing alkalinity (Fig. 9).

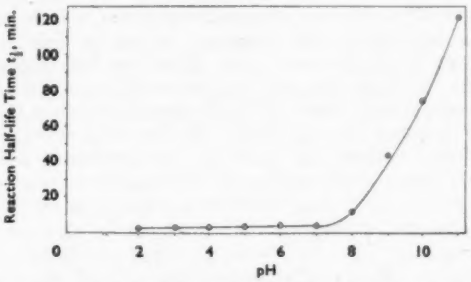


FIG. 9—Relationship between Time for Half Exhaustion of Bath $t_{\frac{1}{2}}$ and pH of Solution for the Reaction between Wool and Chlorine.
Temp. 0°c. 10% Chlorine on weight of wool
Liquor : wool ratio 140 : 1 Fabric rotated at 600 r.p.m.

At pH 8·5 the rate is sufficiently low for the reaction to be controlled by fibre diffusion at room temperature and at stirring speeds and liquor : wool ratios easily attainable in commercial machines. However, above pH 8 chlorine solutions no longer render wool completely unshrinkable (Table III), unless the amount of oxidising agent on the weight of the wool is greatly increased, thus producing unnecessary degradation. The permanganate in the Stevenson–Wolsey process[31] assists the hypochlorite to obtain complete unshrinkability in a pH range where the chlorine firstly does not produce scale stripping and secondly reacts slowly enough to permit uniform treatment in conventional machinery.

The chemical function of the permanganate is to attack a grouping other than the disulphide bond, which is attacked by hypochlorite at all pH values[4], since we believe that attack on the cystine alone does not give unshrinkability except when this reaction is very extensive and results either in the stripping of the cuticle or grave weakening of the whole fibre. Thus, to obtain unshrinkability with oxidising agents the wool molecule has to be ruptured at the disulphide bond and another point which may often be tyrosine[41].

I would like to express my appreciation to the Directors of Messrs. Wolsey Ltd. for permission to publish this paper.

RESEARCH DEPARTMENT
WOLSEY LTD.
LEICESTER

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Discussion

Mr. E. MOLLOY: Is the lecturer aware of the severe effect on fast-dyed cotton yarn of the hypochlorite–permanganate treatment, when goods containing cotton effects are processed? Vat colours of reputed good fastness to chlorine are severely affected in either tone or loss in shade; azoic combinations are also changed.

Dr. ALEXANDER: It is true that some vat colours of reputed good fastness to chlorine cannot be used where accurate shade retention is necessary after application of the hypochlorite–permanganate treatment. Care should be taken to ascertain in each case of failure whether the change is due to the first stage of the process ($NaClO$–$KMnO_4$), or to the second stage of clearing with bisulphite or acid bisulphite. Some dyes will not stand an acid bisulphite clear, but are not so greatly affected by bisulphite alone. In any case, a range of dyes can be dyed which is quite satisfactory in bulk use, when the acid bisulphite clear is being employed.

Mr. E. M. PADGETT: In view of Dr. Alexander's remarks concerning the danger of uneven dyeing after acid chlorination, it is interesting to note that in Yorkshire many pieces are regularly dyed after acid chlorination without encountering undue difficulty.

Dr. ALEXANDER: The dyer who is already dyeing successfully pieces which have been acid-chlorinated will probably admit to considerable difficulties and a percentage of listed or patchy pieces. With the

process I have described he will have less trouble and a greater feeling of safety, since his treatment will be more level and his rate of uptake of dye considerably lower.

Dr. F. J. PILPEL: Is it recommended that the new anti-shrink processes should be applied before or after dyeing?

Mr. B. KRAMRISCH: The lecturer prefers treatment by the Wolsey–Stevenson permanganate–hypochlorite process to be carried out after dyeing, but fears lack of a sufficient range of dyes. According to our tests, however, a full range of dyes of the acid Alizarin and aggregated acid types can be selected, which not only withstand the Wolsey–Stevenson process, but also are of good wet fastness and therefore meet present-day requirements in this regard.

Dr. ALEXANDER: It is recommended that the permanganate–hypochlorite process be applied after dyeing, if this is possible. Apart from all other considerations, the application of the process after dyeing is shorter and therefore more economical, since the goods after clearing are slightly acid and in a condition suitable for normal finishing. If after the anti-shrink treatment they needed to be dyed with some classes of dye, a buffering or neutralising bath would need to be used before proceeding to apply the dye. It should be added that for some dyes this is still the only way to achieve the particular shade required.

Mr. B. KRAMRISCH: Most chlorine non-shrink processes for wool increase its affinity for the majority of wool dyes. Does Dr. Alexander agree that the Wolsey–Stevenson non-shrink process results in decrease in dye affinity, and if so, could he give a theoretical explanation of this behaviour?

Dr. ALEXANDER: The theoretical reason for the decreased dyeing affinity which is undoubtedly brought about by the Wolsey–Stevenson process is not easily seen.

Mr. A. L. KEIGHLEY: Do surface-active agents increase the controllability or levelness of the reaction?

Dr. ALEXANDER: We have not yet determined the influence of surface-active agents on the thickness of the viscous drag layer, but they will probably have an effect. We have some data that the degree of ionisation of the charged group in the wool molecule affects the thickness of this layer, and it may be suspected that surface-active agents, by being adsorbed on to the surface, would modify the charge and in this way produce a similar change.

Mr. D. HAIGH: What is the relative wet tensile strength of acid-chlorinated material?

Dr. ALEXANDER: An increase in dry tensile strength is not always obtained after chlorination, and it would be misleading to quote any figures, since they are highly variable. The change in wet tensile strength after chlorination of yarns also cannot be given without further qualification, since the influence of chlorination on tensile strength varies with the twist in the yarn. The problem posed in this question is well worth further investigation, and I believe that Dr. C. S. Whewell has done a considerable amount of work in this connection.

Mr. J. C. LYSAM: Does treated wool give as efficient insulation properties as untreated wool? Does treated wool wear as long as untreated wool?

Dr. ALEXANDER: We have not been able to detect any changes in the insulating properties of treated wools, but it is very difficult to measure this factor experimentally, and it is possible that a more detailed study would reveal changes. In the same way it is very difficult to assess wearing properties as such, and the only test we have carried out is wet abrasion resistance, which will be related to the wearing properties but not directly proportional to it. Moreover, the importance of high abrasion resistance of wool will be greater with respect to its serviceability in one type of garment than another. We have found that a careful anti-shrink treatment, in particular when employing the hypochlorite–permanganate process, does not appreciably lower the abrasion resistance.

Dr. R. L. ELLIOTT: With respect to statements concerning the liquor–wool movement trials, and the relative merits of Klauder–Weldon and Hussong machines, is it not now necessary to design machines specially for shrink-resist processes? Is there any work in progress in such machine design, e.g. along the lines of the Grid-Flow machine?

Dr. ALEXANDER: I am not aware of any such work.

Dr. J. F. GAUNT: Although the lecture deals only with the chemical treatment of wool, a recent patent (Wolsey Ltd., *B.P.*618,794) claims that the felting properties of wool can be substantially reduced by exposing the wool to ultrasonic radiation. As the effective radius of a 600-watt generator is only 2–3 in., what are the commercial possibilities of this type of instrument and what is the effect of ultrasonic radiation on wool?

Dr. ALEXANDER: There is, in my view, no scope for commercial application of the ultrasonic method for rendering wool unshrinkable with the present generators of ultrasonic waves, since these, as Dr. Gaunt points out, are very expensive and of short range only, especially in water. This is, however, a rapidly expanding field, and in the not too distant future more efficient and effective generators of acoustic waves will almost certainly be developed. In America quite recently great progress has been made with the generation of ultrasonic waves by the piezocrystal method by replacing quartz by barium titanate, which is able to function at much lower voltages than quartz. In this way direct generation in water is made possible.

Mr. J. G. EVANS: Dr. Alexander's statement that the subcuticle has the same chemical composition as the main body of the fibre, but is of a much lower chemical reactivity, is of considerable interest. It would suggest that there is a major difference in organisation as between subcuticle and fibre, the former being much more highly ordered than the latter. This view would fit in with a hypothesis advanced by Mark and Meyer that layers of different crystallisation and orientation as between the surface of the fibre and the core would be expected to affect the resilience of the fibre and contribute to crease-resistance. It is clearly, therefore, of great

importance to determine precisely the chemical and physical state of the subcuticle in relation to the fibre as a whole.

Dr. ALEXANDER: Mr. Evans' inspired suggestion has, within the last few months, been completely verified by experiment[42]. The subcuticle membrane has been shown to be in the β-configuration, unlike the bulk of the wool fibre, which is, of course, in the α-configuration. In the β-form there is more scope for the formation of intermolecular hydrogen bonds than is possible in the α-form, where much of the hydrogen-bonding capacity is taken up in maintaining the intramolecular fold in position. It appears, therefore, that the subcuticle membrane is a tough skin, which from its chemical inactivity can be considered as a protective membrane surrounding the main bulk of the fibre, which is α-keratin and more readily susceptible to attack.

COMMUNICATIONS

The Cellulose–Dye Complex

Part IV—The Polarised Fluorescence from Dyed Fibres

J. M. PRESTON and Y. F. SU

Studies have been made of the relation between the degree of orientation of dyed regenerated cellulose fibres and the degree of polarisation of their fluorescence under various conditions. It is shown that, with certain precautions, the fluorescence method gives a measure of the dichroism of the dyed fibres and is a simple and accurate method of evaluating dichroism.

INTRODUCTION

Using different methods many investigations have been made of the orientations of fibres. Each of these methods has depended on the observation of some anisotropic property which has been correlated with the arrangement of the molecules of the fibres. Of the methods used, one which has been little investigated is that which depends on the polarisation of the fluorescence from dyed fibres. Only Morey[1–3] appears to have published work on this subject. When investigating the closely related dichroic method[4] some time ago, it was considered that the fluorescence method might offer certain advantages[5]. From Morey's work it appeared that the latter method might be independent of the reflection coefficient of the fibres and the thickness of the dyed layer, and might be capable of measurement with simpler optical arrangements. It also appeared that the interpretation of the experimental data might be simpler than in the dichroic method[6].

The aim of the investigation described here was to test the possibilities of the method for measuring the orientations of the molecules of cellulose fibres and to compare the results with those obtained by the dichroic method more thoroughly than had been done by Morey, who had attempted a comparison for one fibre only[7].

A number of suitable fluorescent dyes had been described by Morey[2]. These were of the direct class, which had been earlier shown to have marked dichroic properties[8]. The dichroism of dyed fibres is due to a combination of factors. One is the directional absorption of light by the dye molecules. Another is the directional absorption of the molecules of the dye by the molecules of the fibre[8,9]. Still another factor is the directional arrangement of the molecules of the fibres. Taken together, these factors confer a preferred directional absorption of light on suitably dyed oriented fibres.

The fluorescent light from crystals is highly polarised[10], its plane of polarisation being related to the orientation of the fluorescing molecules. Bowen says further[10]—

> If the absorbing molecule is so oriented that its chromophoric group is parallel to the electric vector of the exciting light, the emitted fluorescence will have the same vector direction . . . Molecules whose chromophoric groups lie at angles to the electric vector are also capable of absorbing, though with efficiencies diminishing to zero at the angle of 90° . . . The fluorescence emitted from these molecules has its electric vector determined by the chromophoric group direction . . .

For a similar reason the light from oriented fibres dyed with suitable fluorescent dyes should also be highly polarised. It might be expected that the anisotropies of the polarisation of the fluorescent light and the dichroic absorption would be similar. With dichroism the anisotropy is conveniently expressed as the ratio of the optical densities for light plane-polarised parallel and perpendicular to the fibre axes. With fluorescence the appropriate ratio is that of the intensities of emitted light plane-polarised parallel and perpendicular to the fibre axes.

EXPERIMENTAL

A supply of the fibres used for the investigation of dichroism, which was reported previously[6], was available for the fluorescence measurements. They were dyed with several fluorescent direct dyes. Measurements were made on fibres dyed with Chlorazol Pink Y (*Colour Index*, No. 225), Diphenyl Fast Yellow (*C.I.* 632), Diazo Fast Yellow (*C.I.* 654), Primuline (*C.I.* 812), and Thioflavine S (*C.I.* 816).

Samples of pure dyes were prepared for colorimetry by making heavy dyeings of the commercial dyes on cuprammonium rayon and washing free from soluble impurities with cold distilled water. The dyes were then extracted with boiling distilled water, and the extracts evaporated to dryness. The ash contents were found to agree with the theoretical values after making allowances for the measured moisture contents. About 0·5 g.

of purified Primuline, for example, could be obtained by two dyeings and two extractions of 10 g. of cuprammonium rayon fibres.

Measurements of the intensities of the fluorescent light were made with two different pieces of apparatus. One of these was the Leitz photometer used in the light reflection measurements described in an earlier communication[11]. In the present work the source of light used was a mercury arc, and the 0·367 μ. band was selected by means of a nickel oxide glass filter. The fluorescent light from the sample was compared with the light from some fluorescent material illuminated by the same source and used as a comparison standard to eliminate the effects of variation in the light source. A filter was used in the path of the fluorescence to cut off any ultra-violet radiation.

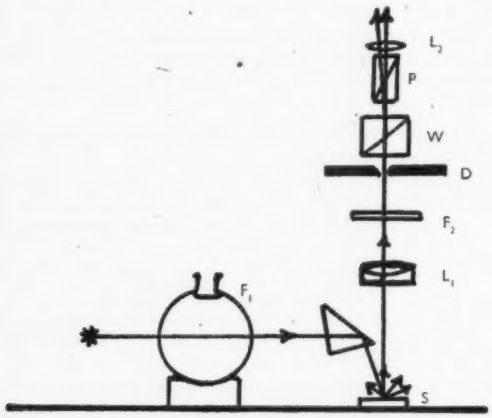

FIG. 1

Later a simpler instrument was used than that just mentioned. It is shown diagrammatically in Fig. 1. In it the exciting light selected by a liquid band-pass filter F_1 was reflected on to the sample S. The fluorescence from this was focussed on to a diaphragm D by means of a lens L_1. A Wollaston prism W above the diaphragm split the light from it into two perpendicularly polarised rays. A polarising prism P was placed above the Wollaston prism and enabled the relative intensities of the two rays to be balanced. This was judged visually by viewing the diaphragm by means of a lens L_2, the relative positions having been so adjusted that the two images of it were contiguous. If the angle of rotation of the polarising prism required for balance is θ, then the relative intensities are given by $\tan^2\theta$. As before, the fluorescence was passed through a filter F_2 to prevent any of the exciting light from reaching the eye.

For a few of the last experiments using the second apparatus, the previous mercury arc was replaced by a point-source mercury arc, and the 0·367, 0·407, and 0·436 μ. lines were filtered through a cuprammonium sulphate solution to remove the longer wavelengths.

With the first apparatus two separate measurements had to be made to get the ratio of the intensities of the two polarised fluorescent beams. With the second apparatus the ratio is obtained directly from a single measurement.

Since it is easiest to make measurements on films instead of fibres, the first experiments were made with dyed cellulose films. Both absorption and fluorescence measurements were made, the former with a Bellingham & Stanley quartz spectrophotometer. The dichroic ratio p was calculated from the comparative optical densities at a number of wavelengths in the near ultra-violet. The polarised fluorescence ratio F was obtained using both pieces of apparatus described above. Some data are given in Table I, which shows that the ratios are similar

TABLE I

Dye	Dichroic Ratio p	Fluorescence Ratio F
Primuline	1·52	1·50
Diphenyl Fast Yellow ...	1·56	1·45

for fluorescence and dichroism for the two dyes. The dichroic ratio is given by $D_{\parallel}/D_{\perp}$, where $D_{\parallel}$ and $D_{\perp}$ are the optical densities parallel and perpendicular respectively to the fibre axes or the axis of extrusion. Similarly, the fluorescence ratio is the ratio of the intensities $I_{\parallel}/I_{\perp}$ where $I_{\parallel}$ and $I_{\perp}$ are the intensities of the rays polarised parallel and perpendicular to the fibre axes as before.

Samples of regenerated cellulose rayon fibres were now dyed with the fluorescent dyes listed above. An attempt was made to measure the concentrations of dye present by stripping with aqueous pyridine and determining the extract with a visual Duboscq colorimeter. This presented no difficulty with the Chlorazol Pink Y, which has an absorption maximum at about 0·53 μ., but dilute solutions of the yellow dyes could not be measured satisfactorily, because their absorption maxima are in the neighbourhood of 0·4 μ., where the eye is insensitive and at the time this part of the work was done only a visual colorimeter was available. For this reason the dyeings with the yellow dyes were described in terms of the dyebath concentrations used in dyeing them.

Five different cellulose rayons were dyed. These possessed a range of orientations from moderately low to very high. The dyed fibres were wound on small glass plates. The winding was done carefully by hand, and successive windings were arranged to be in close contact.

The experimental data for the polarisation ratios for these dyeings are plotted in Fig. 2 and 3. In

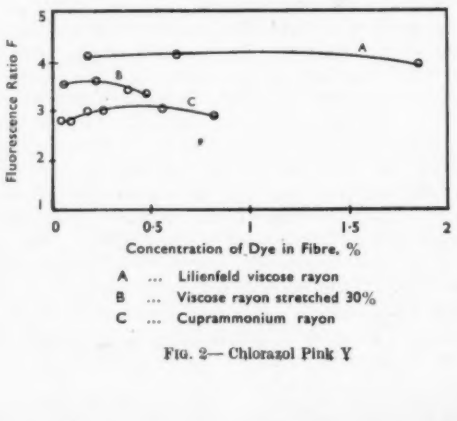

FIG. 2— Chlorazol Pink Y

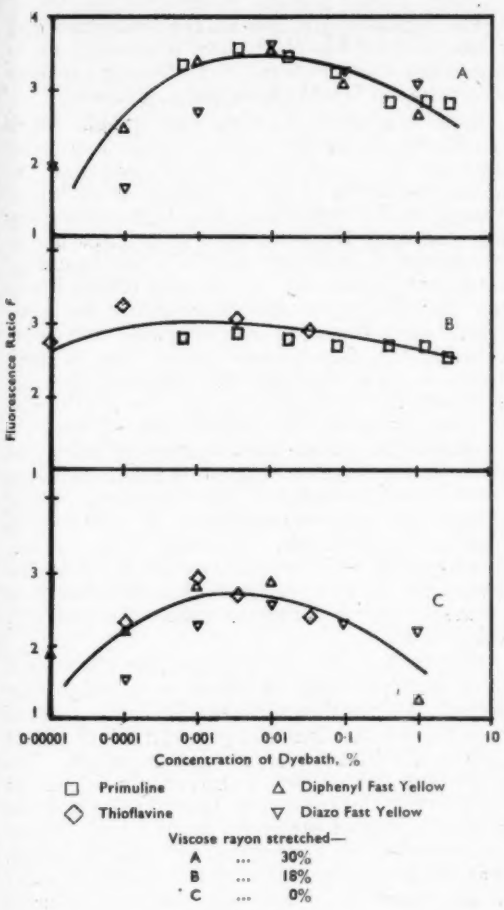

FIG. 3

the case of Chlorazol Pink Y the ratios all show slight maxima. The concentrations of the yellow dyes shown in Fig. 3 are known only very approximately from Neale's generalisation[13] that the equilibrium absorption is roughly proportional to the cube root of the concentration in the dyebath. For convenience, and also so as not to imply any precise knowledge of the concentrations, the polarisation ratios in Fig. 3 are plotted against a logarithmic scale of dyebath concentrations. In all cases the data show maxima at the low concentration side. For comparison the maximum values are set out in column 2 of Table II.

TABLE II

Cellulosic Material	Fluorescence Ratio F	Dichroic Ratio p	$F\,p$
Lilienfeld viscose rayon ...	4·1	8·8	0·47
Cuprammonium rayon ...	3·0	5·3	0·57
Normal viscose rayon—			
Stretched 30%	3·6	4·8	0·74
Stretched 18%	3·1	3·6	0·86
Stretched 0%	2·6	2·6	1·0
Film	1·5	1·5	1·0

DISCUSSION

The fluorescent light from the dyed fibres is mainly polarised in the plane containing the axes of the fibres. The light is thus emitted vibrating in the same plane as that in which it is mainly absorbed. A comparison of the second column of data in Table II with the third column, taken from the previous communication[6], shows that they stand in a similar order except for the cuprammonium rayon, which has a much lower polarisation ratio than would be expected from its anisotropy as measured by dichroism and in other ways (see Part V, p. 361). A further point to be noted is that the ratios are the same for the least oriented materials, but become progressively more divergent the greater the anisotropy. This divergence could clearly be caused either by the dichroisms being too high or by the fluorescence ratios being too low. The latter is believed to be correct, since there is collateral evidence (Part V, p. 361) to show that the dichroic values are approximately correct. If, then, the dichroic values are not too high, this means that the fluorescence ratios are too low for the highly oriented materials.

There are several possible reasons for the low fluorescence ratios, which must be examined in turn. One possibility is the dichroic absorption of the fluorescent light by the dye molecules themselves. It is clear that fluorescent light emitted from the lower layers of dye molecules will have to pass through the upper layers before it can escape and be observable. At first this seemed a plausible explanation, because fluorescent light covers a broad band of frequencies which overlaps, at the high-frequency end, the absorption band of the fluorescing molecules[13]. Further, the absorption of the mutually perpendicular fluorescent rays will be different because of the dichroism. The polarised fluorescent ray vibrating parallel to the fibre axes will be preferentially absorbed. This will reduce the polarisation of the fluorescent light. Whether or not this is an important effect can be ascertained by a suitable experimental test. If the high-frequency end of the fluorescent band is filtered out by means of a suitable filter, then re-absorption of the fluorescent light can be eliminated effectively. Experiments were made to test this hypothesis, but they showed little increase in the fluorescence ratio of filtered compared with that of unfiltered fluorescent light. It thus appears that re-absorption is not an important factor in this case.

Another possibility lies in the way in which light is absorbed and re-emitted. It was considered that this should be examined in more detail than had been done previously.

The intensity of the fluorescent light emitted is proportional to the amount of light absorbed[14], which, in turn, is a function of the concentration; it is directly proportional to the concentration only when this is small, as will become apparent.

If light of unit intensity falls on a transparent layer (say a fibre), the transmitted intensity I is given by—

$$I = e^{-\varepsilon C d} \qquad (ia)$$

where ε, C, and d are the extinction coefficient, concentration, and thickness respectively. For dichroic materials εCd can be resolved into mutually

perpendicular components $(\varepsilon Cd)_{\parallel}$ and $(\varepsilon Cd)_{\perp}$, respectively parallel and perpendicular to the fibre axis. In this case equation (*ia*) becomes—

$$I_{\parallel} = e^{-(\varepsilon Cd)_{\parallel}} \qquad (ib)$$

$$I_{\perp} = e^{-(\varepsilon Cd)_{\perp}} \qquad (ic)$$

The subscripts indicate the direction of vibration of the light.

Now the absorptions for the parallel and perpendicular directions of vibration of the light, $s_{\parallel}$ and $s_{\perp}$ respectively, are given by—

$$s_{\parallel} = 1 - I_{\parallel} = 1 - e^{-(\varepsilon Cd)_{\parallel}}$$

$$s_{\perp} = 1 - I_{\perp} = 1 - e^{-(\varepsilon Cd)_{\perp}}$$

But the intensities of the fluorescence are proportional to the absorptions, and therefore the ratio of the intensities of the polarised fluorescent rays F is given by—

$$F = \frac{s_{\parallel}}{s_{\perp}}$$

Substitution from equations (*ib*) and (*ic*) gives—

$$F = \frac{1 - e^{-(\varepsilon Cd)_{\parallel}}}{1 - e^{-(\varepsilon Cd)_{\perp}}} = \frac{1 - e^{-p(\varepsilon Cd)_{\perp}}}{1 - e^{-(\varepsilon Cd)_{\perp}}} \qquad (ii)$$

where p is the dichroic ratio. Now, expanding the exponential terms on the right-hand side, dividing the numerator and denominator by $(\varepsilon Cd)_{\perp}$, and dividing both sides of the equation by p give—

$$\frac{F}{p} = \frac{1 - \frac{p(\varepsilon Cd)_{\perp}}{2!} + \frac{p^2(\varepsilon Cd)_{\perp}^2}{3!} - \ \ldots}{1 - \frac{(\varepsilon Cd)_{\perp}}{2!} + \frac{(\varepsilon Cd)_{\perp}^2}{3!} - \ \ldots}$$

The R.H.S. is the factor by which F differs from p. In the limiting cases when $p \to 1$ or $(\varepsilon Cd)_{\perp}$ is very small, then the R.H.S. $\to 1$ and $F \to p$. Equation (ii) shows that as $(\varepsilon Cd)_{\perp}$ becomes larger $F \to 1$. Thus if there is a large concentration of dye or a great thickness of the absorbing layer the degree of polarisation will become small. Some intermediate cases have been worked out numerically, and are shown graphically in Fig. 4.

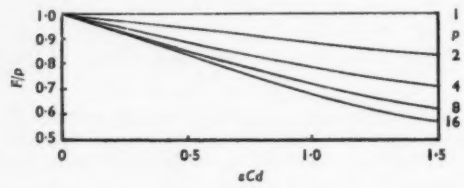

FIG. 4

It thus appears that it is only for low concentrations of dye or for very thin layers that the dichroic ratio and the fluorescence ratio will be equal. The latter should become smaller than the former for greater extinctions, and the effect will be more marked the greater the dichroic ratio. This agrees with the experimental results up to the point when with very low concentrations of dye the polarisation ratio falls. The fall is possibly caused by weak unpolarised fluorescence of impurities in the fibres, which becomes appreciable only for very low concentrations of dye.

The argument up to now has been concerned with a single absorbing layer, and it remains to be considered whether the use of the fibres in a number of superposed layers affects the conclusions.

Apart from about 5% of the incident light, which is reflected at the first surface of the uppermost layer of fibres, all the rest will penetrate the underlying layers of fibres, undergoing successive absorptions and reflections. Any light which is not reflected back from the fibre mass must undergo absorption and give rise to a corresponding amount of fluorescence. All the light reflected from the underlying layers must pass through the upper layers, where it will undergo absorption and excite corresponding fluorescence. In the case of small absorption in a single fibre the amount penetrating successive layers of fibres is greater than in the case of large absorption in a single fibre. Where the absorption in a single fibre approaches unity, the effect of the successive layers is negligible, since there is little transmitted light to undergo either reflection or further absorption. It will be seen from this that the effect of a thick layer of fibres, in comparison with a single layer, is to increase the absorption of the $I_{\perp}$ ray more than the absorption of the $I_{\parallel}$ ray, and thus to reduce the measured value of F.

One method of counteracting the effect of a thick multiple layer of fibres is to reduce the reflections at the fibre surfaces. In the ideal case of no reflection the light can pass through the fibres only in the direction of the incident beam. The effect of multiple layers is then simply to increase the effective thickness of an absorbing layer in the manner discussed earlier for single layers. If the surface reflections are reduced to negligible values, it should be possible, either by reducing the number of superposed fibres and thus effectively reducing the thickness, or by decreasing the concentration of dye, to obtain experimental determinations of F approaching the value of the dichroic ratio and correctly representing the orientation of the molecules of the fibres. One way to reduce reflections is to use a single instead of a multiple layer of fibres; another is to immerse the fibres in a medium of similar refractive index to that of the fibres themselves. Morey in his mass method[3] refers to the use of paraffin oil for immersing a thick layer of fibres, but he does not even hint at the purpose or effect of this procedure.

Experiments were devised to test the effects of reducing surface reflections of the fibres. The values of F were determined using the second apparatus with thick and thin layers of fibres dry and immersed in a medium of refractive index approaching that of the fibre substance. The results were as predicted from the theoretical analysis given above. The optimum conditions were found to be a thin layer of fibres immersed in a suitable non-fluorescing medium of refractive index approaching that of the fibres. The values of F determined under these conditions for four of the fibres of Table II dyed with Primuline are given in Table III.

When the fluorescence ratios are compared with those in Table II it will be seen that the ones of Table

TABLE III

Fibre	Fluorescence Ratio F	Dichroic Ratio p (calc.)
Lilienfeld viscose rayon	9·4	11·9
Cuprammonium rayon	6·7	8·3
Viscose rayon—		
Stretched 30% ...	4·6	5·8
Stretched 0% ...	2·6	3·2

III are nearly all higher. The rise is progressively greater towards the high-orientation end of the series, where the earlier results were clearly too low. This confirmed the theoretical predictions qualitatively.

An attempt was made to calculate how far these new data deviated from the dichroic ratio values in terms of equation (ii) or Fig. 4. For this purpose it was necessary to determine εCd. The concentration C was found by stripping the dye from the fibres by refluxing with 25% pyridine and estimating the amount colorimetrically (refluxing stripped most but not all of the dye from the fibres). The thickness d was obtained microscopically, and the extinction coefficient ε was calculated from a determination of the extinction coefficient in an aqueous solution of the same dye (containing 10% pyridine to prevent aggregation). In an earlier communication[6] the extinction coefficient had been measured for another direct dye on cellulose and had been found to be very close to the extinction coefficient of an aqueous solution of the same dye for the same wavelength after correction for the random disposition of the dye in the solution. It seemed not unreasonable, therefore, to assume that the value of the extinction coefficient of Primuline in cellulose, after allowing for orientation effects, would be similar to its value in aqueous solution. With this assumption and an appropriate correction for the random orientation of the molecules in the dye solution the value of ε for the violet mercury line was found to be $1{\cdot}1 \times 10^3$ when the thickness is expressed in centimetres and the concentration in grams of dye per 100 grams of cellulose and all the dye molecules are considered to be aligned parallel to the electric vector of the exciting light. Under these conditions εCd was about 0·7 for the rayons tested. An inspection of Fig. 4 shows that at this value the observed values of F must be appreciably lower than the corresponding values of p. When the appropriate correction factors were applied, the dichroic ratios shown in the third column of Table III were obtained. These values are all higher than the corresponding values of the dichroic ratios previously determined[6] and reproduced in Table II. The major differences are, however, shown only by the most highly oriented fibres.

The dichroic ratios obtained from the fluorescence measurements are obtained simply and directly, but work which is in progress is required to check the theoretical correction factors corresponding to different values of εCd.

These preliminary studies suggest that the fluorescence method may prove a convenient and simple way of assessing the dichroism of dyed fibres, and from this of obtaining a knowledge of fibre structure on the one hand and of the dyeing process on the other. It should prove applicable to fibres other than cellulosic if appropriate fluorescent dyes are available.

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The Cellulose–Dye Complex

Part V—A Comparison of Orientation Factors derived from Dichroism and other Parameters

J. M. PRESTON and P. C. TSIEN

It is shown that an orientation factor can be derived from the dichroism of dyed fibres. Orientation factors, of certain regenerated cellulose fibres, derived by different methods are compared. Values are quoted for the orientation factors of the same fibres derived from polarised fluorescence, dichroism, birefringence, X-rays, and swelling anisotropy.

INTRODUCTION

In previous communications[1,2], it was shown that the degree of dichroism of cellulose fibres in each case depended upon the orientation of the cellulosic structure. This was equally true whether the phenomena were observed by transmitted or by reflected light. In the last communication[3] (p. 357) it was shown that the dichroism could be derived indirectly from the polarised fluorescence and that it showed a similar symbathy with orientation.

RELATION BETWEEN DICHROISM AND ORIENTATION

The relation between orientation and dichroism can be derived theoretically from a consideration of molecular absorptions. The orientation factor obtained from this relation can then be correlated with orientation factors derived from other fibre parameters. The derivation of the dichroic orientation factor is shown below.

Assume that a dye molecule which is long and polar in nature and exhibits dichroism is embedded

in a transparent cellulose matrix. Assume, further, that it will absorb light vibrating parallel to the long axis of the dye molecule and will transmit all light vibrating perpendicular to the same axis. For light vibrating in other directions the resultant can be obtained by resolving the light into components vibrating parallel and perpendicular to the long axis of the dye molecule. This is shown in Fig. 1, in which the heavy line represents a dye molecule.

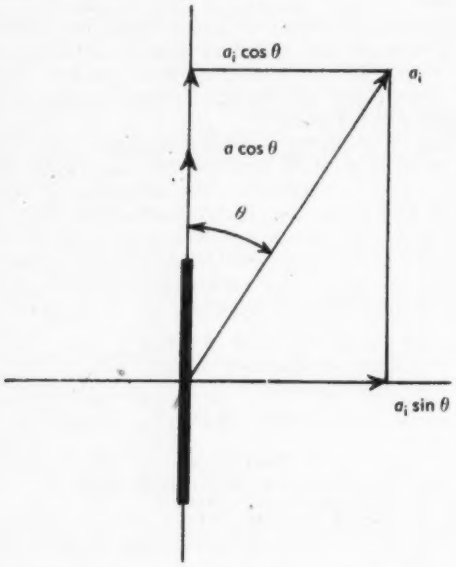

FIG. 1

Let a ray of light, plane-polarised at an angle θ and of amplitude a_1, strike the molecule. The components of the light have amplitudes $a_1 \cos\theta$ and $a_1 \sin\theta$, parallel and perpendicular to the long axis of the dye molecule. After transmission the perpendicular component will be unchanged, but the amplitude of the parallel component will be reduced to $a \cos\theta$ by absorption. Intensity is equal to the square of amplitude[4]; hence the total transmitted intensity I_t is given by—

$$\begin{aligned} I_t &= a_1^2 \sin^2\theta + a^2 \cos^2\theta \\ &= a_1^2 \sin^2\theta + a_1^2 g_0 \cos^2\theta \\ &= a_1^2(\sin^2\theta + g_0 \cos^2\theta) \end{aligned}$$

where g_0 is the fraction transmitted of light vibrating parallel to the axis of absorption and g is the corresponding fraction for light vibrating at any other angle θ. Dividing both sides of the last equation by a_1^2 and substituting g for I_t/a_1^2 gives—

$$g = \sin^2\theta + g_0 \cos^2\theta$$

Subtracting both sides from 1 ($= \sin^2\theta + \cos^2\theta$) gives—

$$1 - g = (1 - g_0)\cos^2\theta$$

From Lambert's and Beer's laws—

$$g_0 = e^{-(\varepsilon cd)_0} \text{ and } g = e^{-\varepsilon cd}$$

where ε is the extinction coefficient, c is the concentration contributed by one molecule, and d is the thickness of the layer. Substituting the exponential terms and expanding them into series gives—

$$1 - 1 + \varepsilon cd - \frac{(\varepsilon cd)^2}{2!} + \ldots = \left[1 - 1 + (\varepsilon cd)_0 - \frac{(\varepsilon cd)_0^2}{2!} + \ldots \right] \cos^2\theta$$

Suppose there are altogether N dye molecules and that the total concentration is C. Then $c = C/N$, and since N is very large, c must be very small, and therefore all the terms of second and higher order can be neglected. The equation therefore becomes—

$$\varepsilon cd = (\varepsilon cd)_0 \cos^2\theta \qquad \text{(i)}$$

When multiplied by log e this gives the optical density for light vibrating in the direction θ.

In a fibre let the angular distribution of the dye molecules round the fibre axis be represented by the intersections of their long axes with the pole sphere,

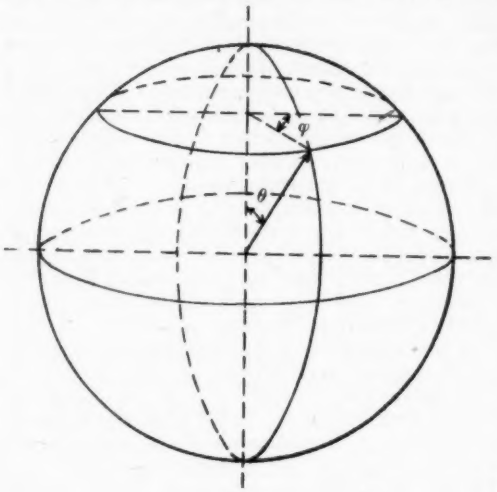

FIG. 2

as shown in Fig. 2, in which θ is the angle between the long axis of the dye molecule and the fibre axis. Following the usual procedure and treating the fibre as a uniaxial structure, the density distribution of these intersections of the pole sphere is a function of θ only, say $f(\theta)$. For random orientation, $f(\theta)$ = constant.

Suppose the pole sphere is divided into zones, each of angular width $\delta\theta$. The number of molecules in any zone is—

$$2\pi f(\theta) \sin\theta \, \delta\theta$$

and the total number of molecules is—

$$N = 2\pi \int_0^\pi f(\theta) \sin\theta \, d\theta$$

The total optical density parallel to the axis for all the molecules in a zone is—

$$(\log e)\,(\varepsilon cd)_0 \cos^2\theta \cdot 2\pi f(\theta) \sin\theta \, \delta\theta$$

The correspondir.g total optical density $D_{\parallel}$ for all the molecules is—

$$D_{\parallel} = (\log e)\,(\varepsilon cd)_0\, 2\pi \int_0^{\pi} f(\theta) \sin\theta \cos^2\theta \, d\theta$$

$$= (\log e)\,(\varepsilon cd)_0 2\pi N \frac{\int_0^{\pi} f(\theta) \sin\theta \cos^2\theta \, d\theta}{N}$$

$$= (\log e)\,(\varepsilon Cd)_0 \frac{2\pi \int_0^{\pi} f(\theta) \sin\theta \cos^2\theta \, d\theta}{2\pi \int_0^{\pi} f(\theta) \sin\theta \, d\theta}$$

$$= D_0 \overline{\cos^2\theta} \qquad \text{(ii)}$$

where D_0 is the optical density if all the dye molecules that contribute to this concentration C are oriented in the direction of light vibration and if $\overline{\cos^2\theta}$ is defined as the ratio of the integrals given above.

For any zone θ, since the dye molecules are uniformly distributed about the fibre axis, the mean optical density per molecule, for light vibrating in a direction perpendicular to the fibre axis in Fig. 2, is given by—

$$(\log e)\,(\varepsilon cd)_0 \sin^2\theta \frac{\int_0^{2\pi} \cos^2\varphi \, d\varphi}{\int_0^{2\pi} d\varphi}$$

$$= \tfrac{1}{2}\,(\log e)(\varepsilon cd)_0 \sin^2\theta$$

Integrating for all the dye molecules in all the zones gives the density $D_{\perp}$ for light vibrating perpendicularly to the fibre axis—

$$D_{\perp} = \tfrac{1}{2}\,(\log e)\,(\varepsilon cd)_0 2\pi \int_0^{\pi} f(\theta) \sin\theta \sin^2\theta \, d\theta$$

$$= \tfrac{1}{2}\,(\log e)\,(\varepsilon cd)_0 2\pi N \frac{\int_0^{\pi} f(\theta) \sin^3\theta \, d\theta}{N}$$

$$= \tfrac{1}{2}\,(\log e)\,(\varepsilon Cd)_0 \frac{2\pi \int_0^{\pi} f(\theta) \sin^3\theta \, d\theta}{2\pi \int_0^{\pi} f(\theta) \sin\theta \, d\theta}$$

$$= \tfrac{1}{2}\,(\log e)\,(\varepsilon Cd)_0 \overline{\sin^2\theta} \qquad \text{(iii)}$$

where $\overline{\sin^2\theta}$ is defined as the ratio of the two integrals, and—

$$D_{\perp} = \tfrac{1}{2} D_0 \overline{\sin^2\theta} \qquad \text{(iv)}$$

From equations (ii) and (iii)—

$$D_{\parallel} + 2D_{\perp} = D_0(\overline{\cos^2\theta} + \overline{\sin^2\theta})$$

Now it can be shown that the sum of the means equals the mean of the sums*; therefore—

$$D_{\parallel} + 2D_{\perp} = D_0 \qquad \text{(v)}$$

* The sum of the mean square cosine and the mean square sine has the form—

$$\frac{\Sigma xy^2}{\Sigma x} + \frac{\Sigma xz^2}{\Sigma x}$$

$$= \frac{x_1y_1^2 + x_1z_1^2 + x_2y_2^2 + x_2z_2^2 + x_3y_3^2 + x_3z_3^2 + \ldots}{x_1 + x_2 + x_3 + \ldots}$$

$$= \frac{x_1(y_1^2 + z_1^2) + x_2(y_2^2 + z_2^2) + x_3(y_3^2 + z_3^2) + \ldots}{x_1 + x_2 + x_3 + \ldots}$$

But $y^2 + z^2 = 1$; hence the sum of the means—

$$= \frac{x_1 + x_2 + x_3 + \ldots}{x_1 + x_2 + x_3 + \ldots} = 1$$

and

$$\frac{D_{\parallel} - D_{\perp}}{D_{\parallel} + 2D_{\perp}} = 1 - \frac{3}{2}\overline{\sin^2\theta} \qquad \text{(vi)}$$

The values of $\overline{\cos^2\theta}$ and $\overline{\sin^2\theta}$ can be found from X-ray data [5,6] and that of $\overline{\sin^2\theta}$ can be found from refractive index measurements[7]. Equation (vi) makes it possible to compare the results of the dichroic method directly with those obtained by these other methods.

Hermans and his coworkers[7] introduced the so-called orientation factor f, which is related to the mean square sine by the relation—

$$f = 1 - \frac{3}{2}\overline{\sin^2\theta} \qquad \text{(vii)}$$

The right-hand sides of equations (vi) and (vii) are similar, and therefore it is possible to put—

$$\frac{D_{\parallel} - D_{\perp}}{D_{\parallel} + 2D_{\perp}} = f \qquad \text{(viii)}$$

Thus an orientation factor can be derived from dichroism measurements, but it must be kept in mind that the significance of the factor may not be the same when derived from different parameters. An orientation factor of this type based on dichroism measurements was first suggested by one of us[1] and was later used by Morey[8].

It is also possible to use $\overline{\cos^2\theta}$ as a measure of orientation, as was previously suggested by one of us[9]. It is now seen that this is as valid as the f factor discussed above. From equations (ii) and (v)—

$$\frac{D_{\parallel}}{D_{\parallel} + 2D_{\perp}} = \overline{\cos^2\theta}$$

The left-hand side of this equation is similar to the first index of orientation proposed in the first paper of this series[1].

In making measurements of dichroism it is often convenient to measure the dichroic ratio, $D_{\parallel}/D_{\perp} = p$, directly. The ratio is a convenient index of the degree of dichroism present, and is related to θ and f by the equations—

$$\frac{p}{p+2} = \overline{\cos^2\theta}$$

$$\frac{2}{p+2} = \overline{\sin^2\theta}$$

$$\frac{p-1}{p+2} = f \qquad \text{(ix)}$$

For completely random orientation it is possible to calculate the mean angle of orientation corresponding to the mean square cosine or sine. When the distribution is completely random and uniform, $f(\theta)$ is constant, and—

$$\overline{\cos^2\theta} = \frac{f(\theta)\int_0^{\pi} \sin\theta \cos^2\theta \, d\theta}{f(\theta)\int_0^{\pi} \sin\theta \, d\theta} = \tfrac{1}{3}$$

That is—

$$\bar{\theta} = 54{\cdot}7°$$

Similarly,

$$\overline{\sin^2\theta} = \tfrac{2}{3}$$

Therefore, from equations (ii) and (iv)—

$$D_{\parallel} = D_{\perp} = \frac{D_0}{3}$$

COMPARISON OF THE ORIENTATION FACTORS FROM DIFFERENT METHODS

The results of orientation measurements using five different methods, viz. X-rays, double refraction, dichroism, polarised fluorescence, and swelling, are collected in Table I. The subscripts to the orientation factors f are used to denote the methods by which they have been derived.

TABLE I

Fibres	Polarised Fluorescence[3]		Dichroism[2]		Birefringence[2]		X-rays[6]	Swelling[10]	
	$I_{\parallel}/I_{\perp}$	f_p	$D_{\parallel}/D_{\perp}$	f_d	$n_{\parallel}-n_{\perp}$	f_o	f_x	B/L	f_s
Lilienfeld viscose rayon	9·4	0·78	8·8	0·78	0·051	0·93	0·95	32	0·95
Cuprammonium rayon	6·7	0·71	5·3	0·59	0·036	0·65	0·88	9·2	0·84
Viscose rayon—									
Stretched 30%	4·6	0·58	4·3	0·56	0·029	0·53	0·80	12	0·88
Stretched 18%	—	—	3·6	0·46	0·025	0·45	—	8·2	0·83
Stretched 0%	2·6	0·43	2·6	0·35	0·019	0·35	0·66	5·2	0·74

The experimental values of the birefringence were converted to oven-dry values by multiplying by the factor 1·17, according to Hermans' data[11]. The value of $n_\varepsilon - n_\omega$* for regenerated cellulose used in evaluating f_o was taken as 0·055[11], though Hermans has given a lower value, 0·050, in his latest book[13a]. The factor f_p was derived from equation (ix), in which p was obtained from equation (ii) of the previous communication (p. 360); f_d and f_o were calculated from equations (viii) and (vii) respectively; and f_x was derived from the mean square sine from X-ray measurements by equation (vii).

The anisotropy of swelling is the ratio of the fractional increase of breadth B to the fractional increase of length L. The factor f_s was calculated from Hermans' equation[7]—

$$f_s = \frac{2\left(\frac{B}{L} - 1\right)}{\frac{2B}{L} + 1}$$

The fluorescence ratios are similar to the dichroic ratios, but after correction in the way indicated previously[3] (p. 361), the values of p derived from the fluorescence measurements are higher than those derived from dichroism. The f_d orientation factors agree with those derived from birefringence except for the highest orientations, for which the f_p values are closer.

The f_s factors agree with the f_x for the most oriented, but diverge most for the less oriented, fibres. The f_s value for highest orientation is near the corresponding f_o value, but the divergence is large for the lower orientations. It has been suggested that this is due to the highly oriented skin present on regenerated cellulose fibres[13], but J. J. Hermans has given an analysis of the problem, from which he concludes that P. H. Hermans' original equations are valid only for very small degrees of swelling[14]. P. H. Hermans has proposed a new empirical correlation between swelling anisotropy and birefringence[12b], in which—

$$\left(\frac{B}{L}\right)^{\frac{1}{2}} = 2f_o + 1$$

A comparison of the data of Table I for B/L and f_o in terms of this correlation is shown in Table II.

It will be seen that there is an approximate concordance of the two columns of values. The viscose fibres are generally higher in the first column of data compared with the second column, whereas cuprammonium is lower. This may be due to the comparative absence of skin on the latter fibres.

TABLE II

Fibres	$(B/L)^{\frac{1}{2}}$	$2f_o + 1$
Lilienfeld viscose rayon ...	3·2	2·9
Cuprammonium rayon ...	2·1	2·3
Viscose rayon—		
Stretched 30%	2·3	2·1
Stretched 18%	2·0	1·9
Stretched 0%	1·7	1·7

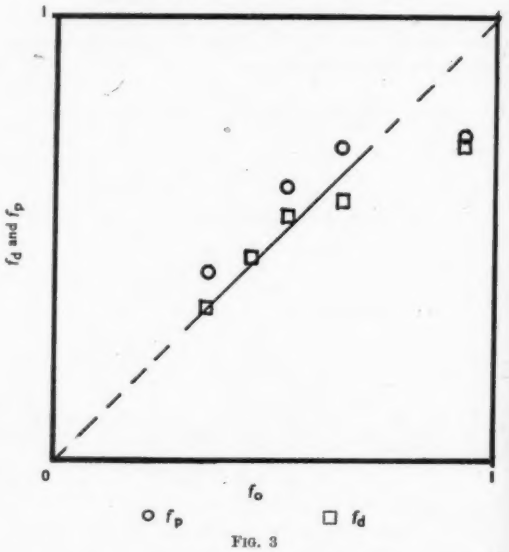

FIG. 3

Values of f_p and f_d are correlated with values of f_o and f_x respectively by the curves shown in Fig. 3 and 4. From the former it can be seen that values of the orientation factors as measured by the birefringence and dichroic methods are proportional, except for the highest ones, which are the least accurate when derived from p, since a small error in $D_\perp$ makes a large change in the ratio p. Otherwise the points lie close to the diagonal with a slope of unity. Since the refractive index of a fibre is determined by all the chain molecules it contains, the approximate equality of f_d (f_p) and f_o means that the numbers of dye molecules absorbed on the

*The symbols n_ε and n_ω represent the refractive indices for the extraordinary and ordinary rays, respectively, for a perfectly oriented fibre.

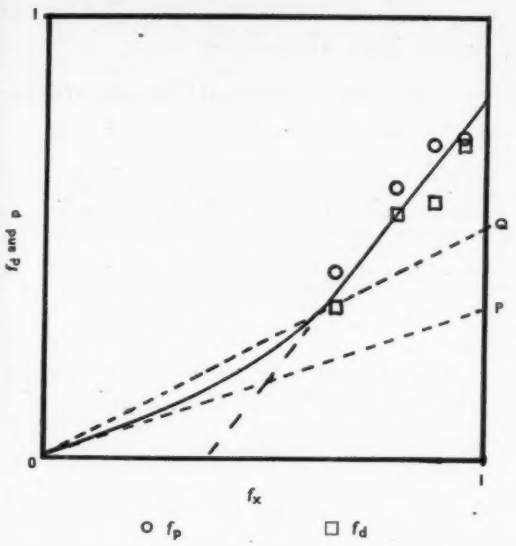

FIG. 4

crystalline regions and those absorbed around and inside the amorphous regions must be approximately in the ratio of the respective numbers of cellulose molecules in the two regions. This conclusion, of course, presupposes that the long substantive dye molecules are attached to the cellulose chain molecules by hydrogen bonds with their long directions parallel, as is now generally believed to be true[15,16].

The relation between f_d (f_p) and f_x (Fig. 4) is approximately linear, but the line does not pass through the origin. If extrapolated it cuts the f_x axis at a value of about 0·4. This is equivalent to saying that a fibre, the crystalline part of which is still 40% oriented, will no longer show dichroic behaviour. For that to be true, the amorphous part would have to be oriented mainly in a direction perpendicular to the fibre axis in order that the average f_d should be zero. This is improbable. The course taken by the extrapolated curved line is the more probable. If Hermans' result[12c] is accepted that the crystalline fraction is about 0·35, then for completely random orientation of the amorphous part, f_d of the fibre must be at least 0·35 f_x, and the extrapolated curve must be bounded at its lower limit by the straight line OP. The upper limit of the extrapolated curve is the straight line OQ, joining the experimental point of lowest orientation to the origin. The slope of OQ represents a crystalline fraction of 0·54.

Let f_{am} denote the fraction of amorphous substance that is oriented axially, and let it be assumed that the fraction of crystalline substance in the fibre is 0·35. Then, by a material balance of the total oriented substance in the fibre, we have the equation—

$$0{\cdot}35 f_x + (1 - 0{\cdot}35) f_{am} = f_d$$

from which we can calculate the fraction f_{am} of amorphous substance that is oriented corresponding to each value of f_x, the fraction of crystalline substance that is oriented. Such values are plotted in Fig. 5. From this it can be inferred that the orientation of the amorphous portion always lags

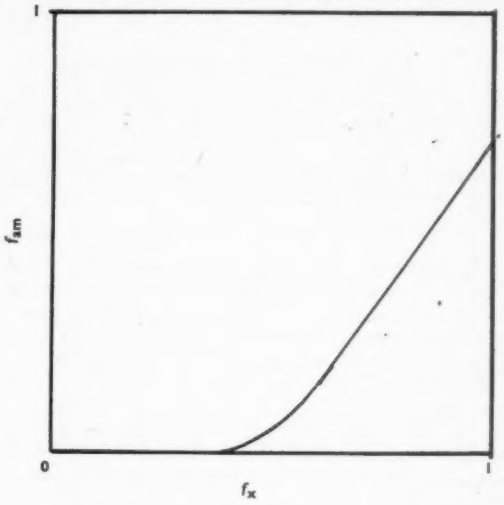

FIG. 5

behind that of the crystalline portion, and the difference tends to become smaller at higher orientations, as Hermans had previously deduced from a comparison of birefringence and X-ray results[11].

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The Diffusion of Direct Dyes into Cellulose

III—The Present State of the Theory and its Practical Implications

J. CRANK

Some recent theoretical papers concerned with the diffusion of direct dyes into cellulose are reviewed. Mathematical solutions of the diffusion equation applicable to dyeing with a restricted amount of dye, as in commercial practice, are presented in a form suitable for calculation. Several examples of calculated rate-of-dyeing curves, suitable for direct comparison with measured rates of dyeing from a commercial dyebath, are shown.

Attempts to provide a quantitative theoretical explanation of the experimental facts about rate of dyeing are discussed. The picture of dye diffusion in cellulose, which seems to be emerging as a result of recent work, is described.

Introduction

The suggestion that dyeing is essentially a diffusion process was first put forward by Neale in 1933[1]. He and his colleagues carried out accurate measurements of the rate of absorption of dye by Cellophane sheet, and similar work was done by Boulton *et al.*[2] on viscose yarn. As a result of these and other experiments the importance of diffusion as the rate-controlling process in dyeing became widely accepted, and many workers have subsequently investigated how the rate of diffusion is influenced by factors such as the concentration of dye and of added salt in the dyebath, temperature, etc.

The position was summarised in 1940 by Boulton and Morton[3] and in 1945 by Standing[4]. In both these reviews it was emphasised that the experimental conditions under which the diffusion of dyes had been studied differed fundamentally from those of the commercial dyebath. Thus in the diffusion experiments a very long bath was used so that the concentration of dye in the bath remained practically constant throughout the dyeing, whereas in commercial dyeing most of the dye initially in the bath is finally transferred to the sheet or fibre and therefore the concentration of dye in the bath falls steadily as dyeing proceeds. This situation arose because the mathematical formulæ available at the time of the early diffusion experiments applied only to the very long, i.e. effectively infinite, dyebath. These formulæ were an essential part of the arguments proving the importance of diffusion, and so the experimental worker was forced to adopt conditions which, no doubt, seemed artificial to the practical dyer.

In their review Boulton and Morton[3] wrote "the diffusion of solute into a rod from a restricted quantity of solution, in which the concentration of solute is reduced progressively during the absorption, presents a case impossible of mathematical treatment." Following this challenging statement a number of papers [5–8] were published in which were derived mathematical formulæ applicable to the restricted or finite dyebath. The first aim of the present paper is to present these new formulæ, and the rate-of-dyeing curves calculated from them, in their simplest form, so that the dyer or the experimental worker can make use of them with a minimum of simple calculation. The mathematical aspects of the finite dyebath are now as fully developed as were those of the infinite bath when the early diffusion experiments were performed. This represents one major advance in recent years.

The other main advance has been towards a fuller understanding of the mechanism of the diffusion process involved in dyeing. When the reviews referred to above were written, it seemed to be accepted that dyeing is essentially a process of free diffusion of dye molecules along water-filled pores within the swollen cellulose, accompanied by adsorption of the dye on the cellulose chains. Recently Neale[9] and the present author[10] have emphasised the importance of the electrical factors inherent in the system. While it is generally agreed that these electrical factors must be allowed for, the quantitative treatment of them presents certain difficulties and has led to some controversy. The second main aim of this paper, therefore, is to review some of the theoretical suggestions that have been made recently, and to indicate what are the points of dispute and agreement and what is the picture of dye diffusion in cellulose which seems to be emerging at the present time.

The present review is confined to theoretical work on dye diffusion, i.e. on the rate at which dyeing takes place. For this reason no reference is made to the several interesting papers published in recent years on the affinity of direct dyes for cellulose and the factors influencing the amount of dye finally absorbed by the cellulose when in equilibrium with the dyebath. Such work is, of course, no less important than diffusion theory, but it lies outside the scope of this review.

I—Mathematical Formulæ and Graphs relating to the Finite Dyebath

The derivations of the following formulæ, expressing the rate of diffusion of a restricted amount of dye or solute into a plane sheet and a cylinder, have been given by Wilson[5] and Crank[8]. The formulæ fall into one or other of two main classes, depending on whether they are particularly suitable for small or large times of dyeing. The following symbols are used throughout—

t ... Time of dyeing

$\bar{D}$ ... Apparent diffusion coefficient (this has the usual dimensions of a diffusion coefficient, e.g. sq.cm./sec.)

l ... Half thickness of sheet

a ... Radius of cylinder

T ... $\bar{D}t/l^2$ for a sheet

$\bar{D}t/a^2$ for a cylinder

M_t ... Amount of dye absorbed by sheet or cylinder at time t

M_∞ ... Equilibrium absorption of dye by sheet or cylinder after infinite time

α ... Parameter expressing the degree of exhaustion of the bath. It is given by the relation—

$$1 + \alpha = \frac{\text{Amount of dye in the bath initially}}{\text{Amount of dye in the sheet or cylinder at equilibrium}}$$

(A) FORMULÆ FOR THE PLANE SHEET

For large times of dyeing—

$$\frac{M_t}{M_\infty} = 1 - \sum_n \frac{2\alpha(1+\alpha)}{1 + \alpha + \alpha^2 q_n^2} e^{-Tq_n^2} \qquad \text{(i)}$$

where the q_n's are the non-zero positive roots of—

$$\tan q_n = -\alpha q_n \qquad \text{(ii)}$$

TABLE I

Roots of Equation (ii)

$\tan q_n = -\alpha q_n$

Exhaustion (%)	α	q_1	q_2	q_3	q_4	q_5
25	3	1·758	4·782	7·896	11·03	14·16
50	1	2·029	4·913	7·979	11·09	14·21
75	$\frac{1}{3}$	2·456	5·233	8·204	11·26	14·34
90	$\frac{1}{9}$	2·836	5·717	8·659	11·65	14·69
99	$\frac{1}{99}$	3·110	6·220	9·331	12·44	15·55
99·9	$\frac{1}{999}$	3·110s	6·221	9·332	12·44	15·55

Numerical values of the q_n's for several different values of α are given in Table I, so that the evaluation of (i) is quite straightforward. Some further values have been given by Carslaw and Jaeger[11]. It may be noted that for a very long dyebath, represented by $\alpha = \infty$, (i) reduces to the familiar solution—

$$\frac{M_t}{M_\infty} = 1 - 8\sum \frac{e^{-(n+\frac{1}{2})^2\pi^2 T}}{(2n+1)^2\pi^2} \qquad \text{(iii)}$$

which is the one used by Neale and the other early workers.

As t and hence T become smaller, it is found that more and more terms of the series in (i) are needed. When more than three or four terms become necessary, it is better to use a solution developed specially for small times. For most values of α the simplest to use is—

$$\frac{M_t}{M_\infty} = (1+\alpha)\left[1 - e^{T/\alpha^2}\operatorname{erfc}(T/\alpha^2)^{\frac{1}{2}}\right] \qquad \text{(iv)}$$

where

$$\operatorname{erfc}(T/\alpha^2)^{\frac{1}{2}} = 1 - \operatorname{erf}(T/\alpha^2)^{\frac{1}{2}}$$

and erf is the error function, which is well tabulated in several standard mathematical tables[12]. For $\alpha = \infty$, (iv) takes the very simple form—

$$\frac{M_t}{M_\infty} = \frac{2}{\pi^{\frac{1}{2}}} T^{\frac{1}{2}} \qquad \text{(v)}$$

If very small values of α are required, which means a very high exhaustion of the bath, e.g. 99% exhaustion or more, there may be a range of values of T in which neither (i) nor (iv) is very convenient, but where the following solution will be useful—

$$\frac{M_t}{M_\infty} = \frac{(1+\alpha)}{\pi^{\frac{1}{2}}}\left(\pi^{\frac{1}{2}} - \frac{\alpha}{T^{\frac{1}{2}}} + \frac{\alpha^2}{2T^{3/2}} - \frac{3\alpha^3}{4T^{5/2}} + \ldots\right) \qquad \text{(vi)}$$

Table II gives values of M_t/M_∞ for different values of T and three values of α to indicate the ranges of T and α over which each of the formulæ is most convenient in use. The calculated rate-of-dyeing curves plotted on a logarithmic time scale in Fig. 1 are in a form suitable for direct comparison with measured rates of dyeing of a sheet from a commercial dyebath.

(B) FORMULÆ FOR THE CYLINDER

There is a set of solutions for the cylinder corresponding to the set for the plane sheet above. For large times of dyeing we have—

$$\frac{M_t}{M_\infty} = 1 - \sum_n \frac{4\alpha(1+\alpha)}{4 + 4\alpha + \alpha^2 q_n^2} e^{-Tq_n^2} \qquad \text{(vii)}$$

where the q_n's are the non-zero positive roots of—

$$\alpha q_n J_0(q_n) + 2J_1(q_n) = 0 \qquad \text{(viii)}$$

J_0, J_1 are the Bessel functions of order 0 and 1 respectively. The required values of q_n satisfying

TABLE II

Diffusion into a Plane Sheet

Values of M_t/M_∞

T	Solution by equation ...	Large α (= ∞) Large t (iii)	Large α (= ∞) Small t (v)	Moderate α (= 1) Large t (i)	Moderate α (= 1) Small t (iv)	Small α (= $\frac{1}{9}$) Large t (i)	Small α (= $\frac{1}{9}$) Small (vi)
0·000 000 04	...	—	—	—	—	—	0·022*
0·000 001	...	—	—	—	—	—	0·104*
0·000 004	...	—	—	—	0·022	—	0·191*
0·000 039	...	—	—	—	0·067	—	0·445*
0·000 156	...	—	—	—	0·128	—	0·637*
0·000 625	...	—	0·028	—	0·234	—	0·794
0·002 50	...	—	0·056	—	0·398	—	0·895
0·010	...	—	0·113	—	0·604	—	0·953
0·050	...	—	0·252	—	0·829	—	0·984
0·100	...	—	0·357	—	0·902	—	0·992
0·200	...	0·504	—	0·950	—	—	0·997
0·300	...	0·613	—	0·984	—	0·999	—

* Calculated from equation (iv) because the series (vi) converges slowly for very small T

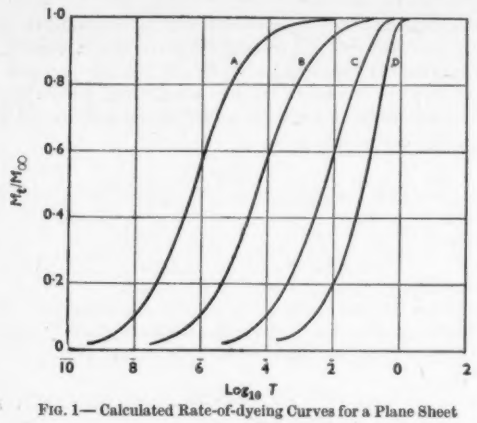

FIG. 1—Calculated Rate-of-dyeing Curves for a Plane Sheet

	α		α
A	$\frac{1}{25}$	C	$\frac{1}{3}$
B	$\frac{1}{50}$	D	1

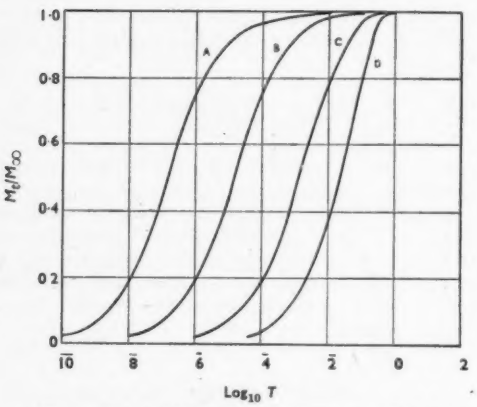

FIG. 2—Calculated Rate-of-dyeing Curves for a Cylinder

(viii) are given for a number of values of α in Table III. For a very long dyebath, for which $\alpha = \infty$, (vii) reduces to—

$$\frac{M_t}{M_\infty} = 1 - 4\sum \frac{e^{-Tq_n^2}}{q_n^2} \qquad \text{(ix)}$$

where now the q_n's are the roots of—

$$J_0(q_n) = 0, \quad q_n > 0 \qquad \text{(x)}$$

TABLE III

Roots of Equation (viii)

$$\alpha q_n J_0(q_n) + 2J_1(q_n) = 0$$

Exhaustion (%)	α	q_1	q_2	q_3	q_4	q_5
25	3	2·641	5·637	8·730	11·85	14·97$_5$
50	1	2·950	5·841	8·873	11·96	15·06
75	$\frac{1}{3}$	3·353	6·248	9·215	12·24	15·30
90	$\frac{1}{9}$	3·637	6·669	9·691	12·72	15·76
99	$\frac{1}{99}$	3·813	6·980	10·12	13·26	16·39
99·9	$\frac{1}{999}$	3·813	6·981	10·12	13·26	16·39

TABLE IV

Roots of Equation (x)

$$J_0(q_n) = 0$$

q_1	q_2	q_3	q_4	q_5
2·405	5·520	8·654	11·79	14·93

The roots of (x) are given in Table IV. Boulton[13] found that equation (ix) represented the dyeing of viscose of round cross-section from an infinite dyebath reasonably well. For small values of T, i.e. in the early stages of dyeing, equation (vii) becomes inconvenient, and should be replaced by the expression—

$$\frac{M_t}{M_\infty} = \frac{1+\alpha}{1+\frac{\alpha}{4}}\left\{1 - e^{4(1+\alpha/4)^2 T/\alpha^2}\,\text{erfc}\left[\frac{2}{\alpha}\left(1+\frac{\alpha}{4}\right)T^{\frac{1}{2}}\right]\right\} \qquad \text{(xi)}$$

where erfc has the same significance as in (iv). For very small values of α there may be a range of values of T over which it is convenient to use the solution—

$$\frac{M_t}{M_\infty} = \frac{1+\alpha}{\pi^{\frac{1}{2}}\left(1+\frac{\alpha}{4}\right)}\left[\pi^{\frac{1}{2}} - \frac{\alpha}{2\left(1+\frac{\alpha}{4}\right)T^{\frac{1}{2}}} + \frac{\alpha^2}{16\left(1+\frac{\alpha}{4}\right)^2 T^{3/2}} - \frac{3\alpha^5}{128\left(1+\frac{\alpha}{4}\right)^5 T^{5/2}} + \cdots\right] \qquad \text{(xii)}$$

When $\alpha = \infty$, there is the simple solution for small values of T, differing from equation (v) for the plane sheet only by a factor of 2, viz.—

$$\frac{M_t}{M_\infty} = \frac{4}{\pi^{\frac{1}{2}}} T^{\frac{1}{2}} \qquad \text{(va)}$$

Table V gives values of M_t/M_∞ for different values of T and three values of α to indicate the ranges of T and α over which each of the formulæ is most convenient. Some examples of calculated

TABLE V

Diffusion into a Cylinder

Values of M_t/M_∞

T	Large α ($= \infty$)		Moderate α ($= 1$)		Small α ($= \frac{1}{10}$)	
Solution by equation ...	Large t (ix)	Small t (va)	Large t (vii)	Small t (xi)	Large t (vii)	Small t (xii)
0·000 000 04	—	—	—	—	—	0·043*
0·000 001	—	—	—	0·022	—	0·191*
0·000 004	—	—	—	0·044	—	0·329*
0·000 039	—	0·014	—	0·128	—	0·634*
0·000 156	—	0·028	—	0·233	—	0·796*
0·000 625	—	0·056	—	0·394	—	0·895
0·002 50	—	0·110	—	0·596	—	0·951
0·010	—	0·215	—	0·786	—	0·979
0·020	—	0·299	0·860	—	—	0·987
0·050	—	0·452	0·933	—	0·994	—
0·100	0·606	—	0·970	—	0·998	—
0·200	0·782	—	0·992	—	0·999	—
0·300	0·878	—	0·998	—	1·000	—

* Calculated from equation (xi) because the series (xii) converges slowly for very small T

rate-of-dyeing curves for a fibre of circular cross-section in baths of different degrees of exhaustion are shown in Fig. 2.

The formal solutions assume a constant diffusion coefficient, which implies a linear absorption isotherm. Some rate-of-dyeing curves have been calculated by the author for non-linear isotherms[6]. When plotted against a logarithmic time scale these are found to differ very little in shape from those of Fig. 2.

II—Theories of the Mechanism of Dye Diffusion

THE MAIN EXPERIMENTAL FACTS

Before discussing the theories of dyeing we must first recall some of the main experimental facts concerning the rate of dyeing for which any complete theory must account.

Neale and Stringfellow[1] dyed Cellophane from an infinite dyebath, and found that for a given salt concentration and temperature the rate of absorption of dye was well described by equation (iii) above. They concluded from this that Fick's law of diffusion was applicable to the dyeing system. The value of the parameter $\overline{D}$, contained in T, in equation (iii), was chosen for each salt concentration to give the best fit between measured and calculated rate-of-dyeing curves, and this is the parameter commonly referred to in dyeing literature as the "apparent diffusion coefficient".

Later Neale and Garvie[14], by studying the way in which the concentration of dye varied through a wad of cellulose sheets at successive times of dyeing, were able to show that Fick's law is not strictly obeyed, but that the diffusion coefficient D_C increases with increasing dye concentration. They concluded that the diffusion coefficient is proportional to the square root of dye concentration. A later refined analysis of the same experimental data[15] suggests the diffusion coefficient to be more nearly directly proportional to concentration. Whatever the detailed relation, however, and it will probably depend on the conditions of dyeing, there is no doubt that the diffusion coefficient increases with increasing dye concentration.

It is now realised[16] that, even for systems in which the diffusion coefficient increases much more violently than is the case for direct dyes in cellulose, the overall absorption–time curve resembles closely that calculated from equation (iii). It is not surprising, therefore, that this is so for rate-of-dyeing curves.

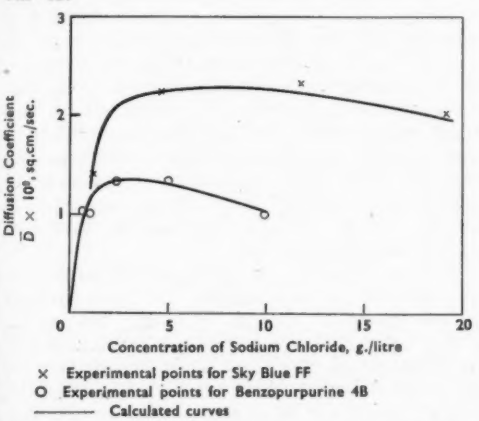

FIG. 3—Diffusion Coefficient of Sky Blue FF and Benzopurpurine 4B in Cellophane at 101°C.

Neale[1] and his colleagues investigated the effect of the concentration of added sodium chloride on the rate of dyeing of Cellophane. Similar work on viscose rayon was done by Boulton and Morton[3]. The results were expressed in terms of the apparent diffusion coefficient referred to above, which means that, in order to study the effect of varying the salt concentration, the variation of the diffusion coefficient with dye concentration was ignored. The circles and crosses in Fig. 3 show Neale's experimental results for the effect of sodium chloride concentration on the rate of diffusion of Sky Blue FF and Benzopurpurine 4B into Cellophane sheet. The curves are calculated and are discussed later.

Standing *et al.*[17] have suggested that the apparent diffusion coefficient is in fact an approximation to a mean diffusion coefficient represented by—

$$\frac{1}{C_e}\int_0^{C_e} D_C \mathrm{d}C$$

where D_C, as we have seen, increases with increasing dye concentration C. In the early part of a diffusion experiment, the concentration C varies from zero at the centre of the sheet or fibre to the equilibrium absorption value C_e on the surface, which is the reason for taking the limits 0 to C_e in the integral. More recently [18] the apparent diffusion coefficient has been shown to differ from the suggested integrated mean value by about 20%, an error which for present purposes we can ignore, so that Fig. 3 can be taken as showing how—

$$\frac{1}{C_e}\int_0^{C_e} D_C \mathrm{d}C$$

varies with salt concentration.

Neale[9] has also measured the rate of passage of dye through a Cellophane membrane from a solution of dye and salt on the one side to a solution of salt only on the other. The effect of the salt concentration on the steady-state rate of diffusion of dye through the membrane is shown in Fig. 4. The rate is immeasurably small in the absence of salt, but rises rapidly with increasing salt concentration to a limiting steady value. There is no tendency to decrease at high salt concentrations as in Fig. 3. The reason for the difference in behaviour between Fig. 3 and 4 is easy to see. If F denotes the rate of flow of dye through the membrane for any given salt concentration, then in the steady state we have—

$$F = -D_C \frac{\mathrm{d}C}{\mathrm{d}x} \qquad \text{(xiii)}$$

and hence—

$$\int_0^l F \mathrm{d}x = -\int_{C_e}^0 D_C \mathrm{d}C = \int_0^{C_e} D_C \mathrm{d}C \qquad \text{(xiv)}$$

where l is the membrane thickness. But in the steady state F is independent of x, i.e. the flow is the same through all sections of the membrane. Hence—

$$\int_0^l F\mathrm{d}x = F\int_0^l \mathrm{d}x = Fl \qquad \text{(xv)}$$

and finally we have—

$$F = \frac{1}{l}\int_0^{C_e} D_C \mathrm{d}C \qquad \text{(xvi)}$$

Hence under identical conditions the curves of Fig. 3 differ from that of Fig. 4 by the factor l/C_e. Since we know that C_e increases with increasing salt concentration, the appearance of the maximum in Fig. 3, but not in Fig. 4, is accounted for.

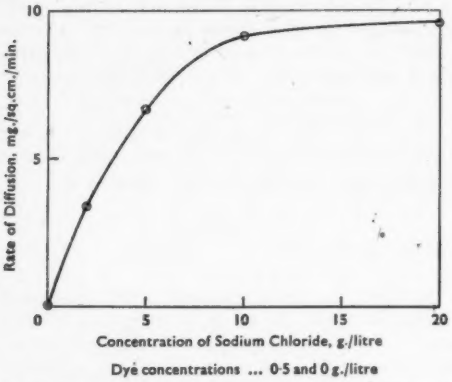

FIG. 4—Rate of Diffusion of Sky Blue FF through Cellophane at 90°C.

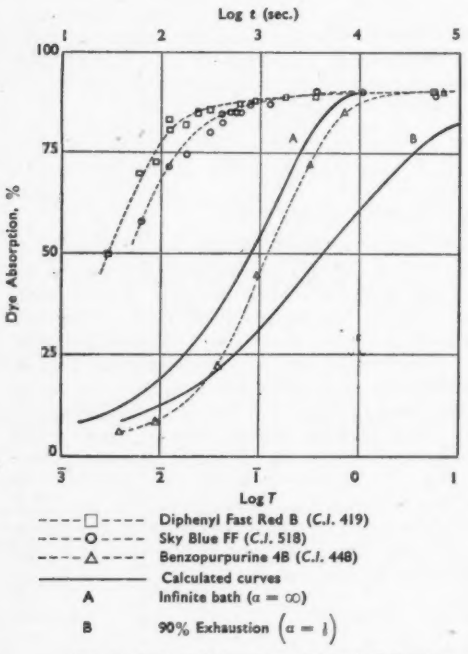

FIG. 5—Rate-of-dyeing Curves for 90% Exhaustion

In Fig. 5 measured rate-of-dyeing curves for three dyes are shown for a bath in which the degree of exhaustion is 90%. The theoretical curve for 90% exhaustion, i.e. $\alpha = \frac{1}{9}$, taken from Fig. 2, is shown for comparison. Only the mean slope of this curve is to be considered, as its position with respect to the logarithmic time axis can be adjusted by choice of the parameter $\overline{D}$. The point of interest is that there are systematic deviations between the slopes of the measured curves in Fig. 5 and that of the calculated one for the same exhaustion. No such marked deviations were found by Neale *et al.*[1] in a precisely similar comparison between observed and calculated curves when an infinite dyebath was used.

Many other factors influence dye diffusion, e.g. type of fibre (whether viscose or cuprammonium rayon, etc.), degree of orientation, and so on. Important though such factors are in practice, from a theoretical point of view they are regarded rather as refinements, for which a quantitative explanation will be possible only when the theory of dye diffusion is much more advanced than at present.

One other highly important variable is temperature. Thus for Fast Red K (0·05 g./litre) in the presence of sodium chloride (5 g./litre) the ratio of the apparent diffusion coefficients at 90°C. and 25°C. respectively is about 64, compared with a corresponding ratio of about 4 for the aqueous diffusion coefficients. The activation energy corresponding to the ratio 64 is of the order of 14 kg. cal. per mole. These figures vary with the salt concentration, however, and at the low temperatures aggregation is probably an important complicating factor.

GENERAL PICTURE OF THE DYEING PROCESS

Although it was possible to describe the overall rates of dyeing from a long dyebath in terms of the simple diffusion equation, it was soon realised that some complicating factors must be present. In order to take into account the affinity that the dye shows for the cellulose, the diffusion must be accompanied by absorption, and this idea, combined with other evidence on the nature of the water-swollen cellulose, led to the following picture of the dyeing process.

In the amorphous region between the crystallites in water-swollen cellulose, the cellulose chains are considered to form a three-dimensional network of water-filled pores or capillaries. Single dye molecules are assumed to diffuse in solution along the pores and to be simultaneously adsorbed on the cellulose chains, so that dyeing is represented as a process of diffusion in an absorbing medium. A systematic study of the quantitative implications of this theoretical model and of the extent to which it can be used to explain experimental data was made by Standing *et al.*[17].

It may be remarked in passing that, while the above picture is convenient for description, it is not essential to the following discussion. Whether the diffusion really occurs unhindered in water along pores which are large compared with a dye molecule or whether it is better to think of diffusion through a viscous water–cellulose solution, the mathematics remains the same, though the physical significance of some parameters may

differ. The essential postulate is that dye molecules can be in two states, namely (i) free to diffuse, and (ii) attached to cellulose chains and immobilised. Certainly, if published estimates of pore size are meaningful, the figure of 20–30 A. quoted for their diameter is hardly in keeping with the free diffusion in water of a dye molecule measuring 30 × 10 × 8 A.[3].

This general picture of dyeing has been criticised recently by Harrison[19], who considers that the idea of dye molecules becoming attached to the cellulose chains is fundamentally wrong. He still prefers the idea, which he himself put forward in 1911, that the colour ions of direct dyes have an affinity for each other, which under dyeing conditions causes them to form aggregates or micelles within the pore spaces in the cellulose. In putting forward indirect experimental evidence to support his aggregation theory, however, he makes no reference to Morton's[20] work on the dichroism of dyed fibres, though this appears to support very strongly indeed the idea that the dye is attached to the cellulose chains in the form of single molecules.

DYEING CONSIDERED AS DIFFUSION IN AN ABSORBING MEDIUM

Diffusion in an absorbing medium can be represented by the equation for simple diffusion provided a diffusion coefficient varying in a certain way with concentration is used. Thus, if C represents the overall concentration of dye within the cellulose, expressed per unit overall volume, C_p the concentration of free dye in solution in the pores, per unit volume of water, and v the volume fraction of water-filled pore space, then it can readily be shown[17] that diffusion with absorption is represented by the usual diffusion equation with a variable diffusion coefficient D_C given by—

$$D_C = D_p v \frac{dC_p}{dC} \qquad \text{(xvii)}$$

D_p, the coefficient of diffusion of the free dye along the pores in the absence of absorption, being assumed constant. It is further assumed that the dye molecules adsorbed on the cellulose chains do not diffuse. Some support is given to this last assumption in the paper by Standing *et al.*[17]. Local equilibrium between free and adsorbed dye is considered to be reached instantaneously.

If C_p is identified with that concentration in the dyebath which would give the same overall concentration of dye C within the cellulose, then the relation between C and C_p is that of the absorption isotherm relating the overall concentration of absorbed dye in the cellulose to the external dyebath concentration with which it is in equilibrium. The isotherms of many direct dyes fit the Freundlich equation, so that the relation between C and C_p takes the form—

$$C = RC_p^m \qquad \text{(xviii)}$$

where R and m are constants, m lying between 0 and 1·0. On substituting from (xviii) in (xvii), we find that the diffusion coefficient D_C is proportional to $C^{(1-m)/m}$, and therefore increases as C increases. This is qualitatively in agreement with the results of the wad experiment[14] referred to earlier (p. 369). The exponent in the absorption isotherm relating to the dye used in the wad experiment has the value $m = \frac{1}{3}$, which implies a diffusion coefficient varying as C^2, compared with C or C^3 found experimentally. Thus, although the simple diffusion-with-absorption model leads to deviations from Fick's law which are in the same direction and of the same algebraic form as the deviations found experimentally, there is no quantitative agreement in this particular case between measured and theoretical values of the exponent m.

If we accept the approximate statement that the apparent diffusion coefficient $\bar{D}$ can be identified with—

$$\frac{1}{C_e}\int_0^{C_e} D_C dC$$

then it is easily found by substituting under the integral for D_C from (xvii) that—

$$\bar{D} = D_p v \frac{C_{p0}}{C_e} \qquad \text{(xix)}$$

Here C_{p0} is the concentration in the pores when the equilibrium absorption is C_e. In studying experimentally the salt dependence of the apparent diffusion coefficient, the concentration of dye in the bath is kept constant; i.e. in equation (xix) C_{p0} remains constant while C_e changes with the salt concentration. Now the equilibrium absorption C_e increases steadily with increasing salt concentration, dye concentration remaining constant[1], and therefore we see at once from (xix) that the apparent diffusion coefficient should decrease with increasing salt concentration. Reference to Fig. 3 again shows that this is so only at high salt concentrations, and that at low salt concentrations the theoretical prediction breaks down completely.

ELECTRICAL FACTORS

The facts that the behaviour of the apparent diffusion coefficient at high salt concentrations predicted by the diffusion-with-absorption model is in qualitative agreement with observation, but that the theory fails completely at low salt concentrations, suggest that some neglected factor in the system becomes of major importance at low salt concentrations. In developing the diffusion-with-absorption theory no allowance was made for the electrochemical nature of the system, i.e. for the facts that the dye molecules are ionised and that cellulose is known to exhibit a negative charge in water. In the case of anionic direct dyes the diffusion of the organic anion is the interesting feature, and the charge on the cellulose will be increased as the negatively charged dye ions are adsorbed first on the outer surface and later throughout the cellulose. It seems reasonable to expect that this negative charge will repel other negatively charged ions tending to diffuse into the cellulose. Also, since we know that the height of the potential barrier, and hence the repelling effect associated with a given charge, decrease rapidly with increasing salt concentration[21], this appears to offer an attractive explanation of the sudden rise in diffusion rate at low salt concentrations, though it is complicated by the fact that the charge itself increases with increasing salt concentration. At

high concentrations of salt the electrical barriers become negligible and absorption becomes the controlling feature. The quantitative introduction of electrical factors into the diffusion-with-absorption theory presents certain difficulties, however.

In the first place, when the ionic nature of the system is considered, it is no longer permissible to assume that in the final equilibrium state the concentration of dye in the pores is the same as in the dyebath. Theories of equilibrium absorption are based on the assumption that the pore concentration is less than in the dyebath, the ratio being calculable from the Donnan equations for membrane equilibria or from Boltzmann's equations for the distribution of ions in an electric field. These theories further assume the cellulose region to be an equipotential one.

The remaining assumption, which has an important bearing on the diffusion problem, is that the partition factor between absorbed and free dye *within* the cellulose region is independent of both dye and salt concentrations. To assume the partition factor to be independent of dye concentration means that in equation (xvii) above dC_p/dC is constant, and hence the diffusion coefficient becomes independent of dye concentration. We therefore have to find another explanation of the concentration dependence of the diffusion coefficient observed experimentally. It may be that the concentration dependence results from the interaction between the diffusing dye molecules and those adsorbed on the cellulose chains, or it may be that the assumption of the equilibrium theories needs revision. At the moment we can only note the inconsistency.

The present author[10] found that to assume the internal partition factor to be independent of salt concentration would lead to an apparent diffusion coefficient independent of salt concentration, and that, if the picture of free diffusion in an equipotential region is to be maintained, the variation of the apparent diffusion coefficient must be reflected in a variation in the partition factor with salt concentration. If such a new assumption is made, equation (xix) takes the modified form[10]—

$$\overline{D} = D_p r f \frac{C_b}{C_e} \qquad \text{(xx)}$$

where f is the fraction of dye molecules able to overcome the potential barrier due to the charge of the cellulose and the adsorbed dye ions, and hence enter the cellulose region. Here C_b is the dye concentration in the bath, so that C_e is related to C_b through the absorption isotherm. The factor f involves the charge density on undyed cellulose e_c and the total surface area A (internal + external) of the cellulose. By suitable choice of these parameters the observed salt dependence of the apparent diffusion coefficient shown by the curves of Fig. 3 can be reasonably well accounted for. The mean values of the parameters emerging from this analysis seem quite reasonable. Thus Morton[22] has pointed out that the value for A, namely, $4{\cdot}6 \times 10^8$ sq. cm. per 100 g. of cellulose, is in good agreement with that calculated from the pore diameter of 30 A. measured by pumping water through Cellophane, which, however doubtful, is at the moment the only direct indication of pore size. Incidentally, this agreement is not referred to by Harrison[19] when he criticises the figure of $4{\cdot}6 \times 10^8$ as too large. Morton also calculates that the value for e_c of 4050 e.s.u. per sq. cm. is roughly the charge to be expected from the carboxyl groups of the cellulose if these are assumed fully dissociated.

The parameter D_p represents the diffusion coefficient of dye through cellulose when the effects of adsorption and electrical barriers are allowed for. It is of interest that the values of D_p for three dyes were all about 10^{-5} sq. cm./sec., which is of the order of the aqueous diffusion coefficient of direct dyes.

The equations and parameters[10] used to describe the salt dependence of the apparent diffusion coefficient at constant temperature are also found to account satisfactorily for the temperature dependence (salt concentration remaining constant) above 60°C. Below this it is probable that discrepancies arise, at least in part, because of aggregation of the dye, which was not allowed for in the theoretical treatment.

REVISED PICTURE OF DYE DIFFUSION

Failure to account for the facts of dye diffusion, in terms of the model and assumptions previously found adequate to provide a basis for equilibrium theories, suggests that the picture of the cellulose region needs revision. Although the assumption of an equipotential region may be tolerable for theories of equilibrium absorption, it may not be good enough to account for diffusion behaviour, which is likely to be much more sensitive to local variations within the cellulose. This, incidentally, seems to be a very good reason for studying diffusion even though the supposedly simpler equilibrium problem is not fully understood.

It has been suggested[4] that the network of cellulose chains may impede the diffusion of the dye. The idea of hindered diffusion is, as we have already noted, somewhat to be expected if the estimated diameters of 20–30 A. are correct. Furthermore, if the cellulose chains are as close as this, the diffusing molecules may well have to surmount a number of successive electric potential barriers, associated for example with the carboxyl groups of the cellulose and/or other dye ions attached to the cellulose. This sort of picture would allow the factor f in equation (xx) to be associated with the diffusion coefficient D_p, expressing mobility along the pore, rather than with the partition factor. The equation would remain unchanged in form (though the detailed calculation of f might differ) if, as Standing[23] pointed out, the pore concentration of free dye were equated to the dyebath concentration. This seems unlikely to be true, and in the equilibrium theories, at least a part of the free dye in the pores is assumed to obey the Donnan equations. The only attempt so far published to test the point by direct experiment[24] led to considerable controversy, however, but the evidence suggested that the Donnan equations could not account completely for the ion distribution. There is thus no point at the moment in complicating equation (xx) further till more evidence on the ratio of

internal and external concentrations is available. Neale[25] has recently suggested that the diffusing molecule must surmount a succession of electrical barriers, probably due to carboxyl groups, but he considers it essential to assume that this diffusion takes place in the adsorbed layer, i.e. along the cellulose chains and not between them, though the arguments advanced seem a little obscure. However, there seems little doubt that electrical repulsion in some form is responsible for the behaviour of the diffusion coefficient at low salt concentrations.

It has always been realised, of course, that the idea of water-filled permanent channels or pores in the cellulose is much over-simplified and of limited application. The desirability of adopting a picture in conformity with recent advances in knowledge of molecular behaviour and the mechanism of swelling of high polymers has been stressed by Entwistle[26]. He suggests that in the water-swollen regions the cellulose chain segments are in a state of continuous motion under the action of thermal agitation. Such regions can be regarded as "solutions" of cellulose and water in which the cellulose segments have a limited mobility between the more highly ordered unswollen regions. The diffusion of a dye molecule into such a structure can therefore be considered as diffusion into a viscous liquid, and the rate of dyeing will be influenced by factors which affect the "molecular viscosity" of this liquid. We have seen that the concept of electrical potential barriers must be added to this viscous solution picture. The position at the moment, therefore, may be summarised by saying that the old picture of free diffusion along water-filled pores may have to be replaced by one in which the dye molecule is pictured as diffusing through a cellulose–water solution and jumping over a succession of potential barriers due to local concentrations of charge. Simultaneous adsorption of dye on the cellulose chains will still occur, of course, and there may be diffusion in the adsorbed layer. Whilst this model seems qualitatively satisfying, and offers a possibility of clearing up much of the inconsistency that has arisen in dyeing theories, it is nevertheless a much more difficult model to handle quantitatively than the old water-filled pore model. Diffusion of a non-ionised molecule through the water–cellulose solution may be somewhat slower than through pure water, but most of the hindrance to diffusion of an ionised dye molecule seems likely to be electrical in origin. The difficulty of calculation lies in lack of knowledge about spacings of carboxyl groups and adsorbed dye ions, etc. in the amorphous region of swollen cellulose. The spacings will in fact be changing continuously with time.

It seems likely that, before our knowledge of the mechanism of diffusion can be extended appreciably further, many new diffusion measurements are needed. Particularly valuable would be data on the effect of dye and salt concentrations and temperature on diffusion rate (*a*) in celluloses of zero and intermediate carboxyl contents; (*b*) when the diffusing dye is non-substantive, so that complications of absorption are removed; (*c*) when the diffusing molecules are comparable in size with a dye molecule but non-ionised.

THE FINITE DYEBATH

We saw in Fig. 5 that the calculated curve did not agree particularly well with any of the measured rate-of-dyeing curves for a finite dyebath. Part of the discrepancy may be due to the neglect of electrical factors in deriving the formulæ set out in Part I of this paper, where we assumed that all molecules in the bath could enter the cellulose. If, however, we take the view that, when the cellulose is placed in the dyebath, an electrical potential barrier is developed at its surface due to the combined charge of the undyed cellulose and the dye instantaneously adsorbed on the surface, then only a certain fraction of the dye ions in the bath are able to surmount this barrier and enter the cellulose region. This fraction will increase as dyeing proceeds, i.e. as the concentration of adsorbed dye on the outer surface and hence the surface charge and potential decrease. The effect of such an electrical barrier is therefore to make the bath appear less finite than it really is. It is interesting to see in Fig. 5 that the measured curves agree much better with the theoretical curve for an infinite bath than with that calculated for 90% exhaustion. The equations describing rate of dyeing from a finite bath with electrical factors included have been derived by the author[15], but no solutions have yet been evaluated. Further experimental measurements under different conditions of dyeing are desirable, in order that, if deviations from the theoretical formulæ are confirmed, they can be studied more systematically for both the plane sheet and the cylinder. Probably such deviations will occur under certain conditions of dyeing but not under others.

Now that the most obvious property of the commercial dyebath, viz. its finiteness, can be handled mathematically and allowed for, it should be possible and profitable, to both the theoretician and the dyer, to consider other factors which may influence rate of dyeing in practice. A start in this direction has already been made by Armfield[27], who has made a preliminary investigation of the effect of the rate at which salt is added to the dyebath, when it is added continuously as dyeing proceeds.

COURTAULDS LIMITED
MAIDENHEAD
BERKS.

(*Received 1st February 1950*)

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A Note on the Formation of Polymers in Wool

C. Fearnley and J. B. Speakman

When wool fibres are impregnated with a dilute solution of ferrous ammonium sulphate and then treated with a mixture of hydrogen peroxide and methacrylamide in an atmosphere of nitrogen at 50°C., internal deposition of polymer takes place extremely slowly and reproducible results are difficult to obtain[1]. These difficulties seem to be due to reaction between hydrogen peroxide and the monomer during uncontrolled times of standing before addition to the wool, because more rapid and reproducible deposition of polymer has now been realised simply by adding the solution of methacrylamide to the impregnated wool before the hydrogen peroxide.

In an earlier paper on this subject[1], a general method of forming polymers inside wool fibres has been described. This consists in impregnating the fibres with a dilute solution of ferrous ammonium sulphate and then applying a mixture of monomer and hydrogen peroxide in an atmosphere of nitrogen. Preferential internal polymerisation is brought about by the free hydroxyl radicals which are formed inside the fibres when the hydrogen peroxide encounters the iron. In this way it was found possible to deposit as much as 41% of polymethacrylic acid in an all-wool flannel in 50 min. at 25°c., but difficulties were encountered with methacrylamide. Only 14·4% of polymer was deposited in 6 hr. at 50°c. under corresponding conditions. The slowness of the polymerisation process is hardly compatible with free radical initiation, and it seemed possible that this, and the non-reproducibility of the results, might be due to removal of hydrogen peroxide by reaction with the methacrylamide[2] during uncontrolled times of standing prior to contact with the wool. Further experiments, in which methacrylamide and hydrogen peroxide were added separately to the wool, have therefore been carried out.

From the same supply of flannel as before[1], 2·5-g. patterns were prepared and purified by extraction with alcohol and ether in the usual way. The patterns were then conditioned at 65% R.H. and 22·2°c. before being weighed ready for use. Each pattern was afterwards immersed in 20 c.c. of a 0·1% solution of ferrous ammonium sulphate in 0·1 N. sulphuric acid for 2 hr. at 25°c., pressed between filter papers, dried in a stream of warm air, and transferred to the reaction tube. The latter was then evacuated and filled with oxygen-free nitrogen, which was allowed to stream through the apparatus after the addition of 10 c.c. of a 20% solution of methacrylamide, previously freed from oxygen. After 15 min., 1 c.c. of 0·2-vol. hydrogen peroxide was added to initiate polymerisation, and the reaction was allowed to proceed for the desired time at 50°c. The pattern was then removed, washed in running water overnight, centrifuged, conditioned, and reweighed. The gains of weight of patterns treated in this way for different times are given in Table I. Several such experiments were carried out, and in all cases it was found that large amounts of polymethacrylamide could be deposited in the fibres in a few minutes when the monomer was added before the hydrogen peroxide.

Table I

Time of Treatment (min.)	Increase in Weight (%)
5	22·4
15	36·4
30	41·4
60	37·7

Besides ensuring more rapid polymerisation, the revised procedure gives more reproducible results, as is indicated by the following experiments. Two 2·5-g. patterns of flannel were impregnated with ferrous ammonium sulphate solution in the usual way, and then immersed in a solution of methacrylamide (4 g.) in 25 c.c. of a 0·5% solution of Lissolamine V (ICI), the latter being introduced as a wetting agent. A stream of oxygen-free carbon dioxide was passed through the apparatus before and during the reaction, which was initiated with 2·5 c.c. of 0·2-vol. hydrogen peroxide. Polymerisation was allowed to proceed for 2 hr. at 50°c., and the patterns were then washed in running water, conditioned, and reweighed. Two other patterns were subsequently treated in the same way, and the results of both experiments are given in Table II.

Table II

Series	Increase in Weight (%)
1	59·9
	60·8
2	52·3
	51·2

The success of the above procedure in giving rapid internal formation and deposition of polymer removes the chief obstacle to the development of methods for reinforcing wool fibres by cross-linking the chain molecules of the polymer and the wool with formaldehyde.

The authors are indebted to the International Wool Secretariat for grants in aid of this investigation.

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CORRESPONDENCE

The Editor does not hold himself responsible for opinions expressed by correspondents

The Standardisation of Dyes

The Editor

SIR,

Mr. Shackleton in his lecture on *The Standardisation of Dyes*[1], after stating that he had no personal experience of those almost legendary war years (World War I) of the dye industry, said he had gathered the impression that standardisation in those days was very undeveloped and rather at the mercy of the errors and enthusiasm of infancy. Later he says it was only in the early 1920s that the term "to standardise" acquired a respectable significance.

May I, as one who joined the dye industry in 1899, be allowed the opportunity to repudiate the imputations made by Mr. Shackleton, who, I think, in future should check his evidence before publicising such misstatements based on ignorance. If he were to be believed, it would have to be accepted that Badische, Meister, Bayer, Berlin, Cassella, Leonhardt, Kalle, Ciba, Geigy, and Sandoz did not standardise their products previous to 1914 in as efficient a manner as post-1920. Colour users who have experience of pre-1914 and post-1920 standardisation of commercial deliveries will confirm my statement that the standardisation of pre-1914 commercial deliveries was fully equal to that obtaining to-day. I, myself, standardised dyes at Turnbridge Works, Huddersfield, from 1910 to 1920, including union blacks containing six different dyestuffs. I must, therefore, ask to be allowed to repudiate in the strongest possible terms the allegations made by Mr. Shackleton.

Mr. Shackleton is clearly unaware that the shortage of dyestuffs obtaining after 1914 produced the condition that it was frequently more profitable for a dyer to become a "spiv" than to use his stock of dyes in his ordinary commercial practice. The condition became so fantastic that Chicago Blue 6B bought for 11d. per lb. was sold in Bradford for 90s. per lb. Some colour users found it so profitable that they actually employed a traveller to sell the diluted dyes referred to. Such sales were not made by the reputable British dyemakers, who maintained their standards as well as they are maintained to-day. Short supplies in any market always breed "spivs".

In my day each batch of Chlorazol Black E was tested separately, and those batches containing impurities were segregated and placed in quarters in which their use was not detrimental, but obviously they were not sold for union dyeing or burl dyeing. The industry had not to wait until post-1920 to learn that little bit of common sense.

It would be amazing if thirty years later no progress in methods of standardisation had been made, such as the Marney machine, which is excellent for use in a standardising department, whilst the Hardy spectrophotometer is equally admirable but can never be a substitute for human intelligence. No instrument yet on the market can tell you from a solution whether the batch being tested dyes at the same rate as the standard type. A dye test must still be the final arbiter of those dyestuffs which are standardised for normal methods of application.

Yours faithfully

C. M. WHITTAKER

"WEAPONNESS"
MANOR ROAD
CHEADLE HULME
CHESHIRE

4th May 1950

[1]Shackleton, J.S.D.C., **66**, 221 (April 1950).

The Editor

SIR,

May I be allowed to point out to Dr. Whittaker that, because of the active study of standardising problems covering the major part of 31 years spent in the dyestuffs manufacturing industry, I can hardly be ignorant of the standards achieved prior to 1914, of the effects of the dyestuffs famine of World War I, or of the growth and progress of both maker and user industries since then.

The published text of the above lecture deals only, and obviously I think, with the unfortunate impressions left by the dyestuffs famine of World War I, and describes steps taken since to achieve a more scientific control of both manufacture and standardising, and neither word nor intent carries any imputation.

I have no doubt that the reputable firms quoted by Dr. Whittaker did standardise their products in a reputable and reasonably efficient manner prior to 1914, and still do so to-day, but I must continue to assert that the standards accepted in those days would not be accepted by either manufacturing or using industries to-day.

As no-one has done more than he to draw the attention of manufacturers to the inconsistency of their products, I believe that, if he were asked to accept deliveries of pre-1914 commercial qualities, his reaction would be immediate and characteristic.

For this reason I find it difficult to reconcile his statement, that standardising of pre-1914 commercial deliveries was fully equal to that obtaining to-day, with his statement, in the last paragraph of his letter, that it would be amazing if 30 years later no progress had been made.

While Dr. Whittaker's defence of the reputable manufacturer is generous, he would be the first to point out that the first step to the progress made during the past 30 years has been the recognition of errors and imperfections of the past, and I have no doubt that he will continue to draw attention to any that might come to his notice.

Yours faithfully

R. W. SHACKLETON

HEXAGON HOUSE
BLACKLEY
MANCHESTER

17th May 1950

ERRATUM

Report of the Committee on the Dyeing Properties of Wool Dyes (J.S.D.C., **66**, 213–221 (April 1950))—

On p. 214, in the paragraph beginning near the middle of the first column, it is a *minimum* degree of exhaustion of 90 ± 2·5% that has been chosen arbitrarily in order to select the dyeing method most suitable for use with the dye under test.

On p. 221, in the second column, the optimum dyeing method for Xylene Fast Blue P (S) is Method IV, not III. Thus "**IV 89·6 5·9 3**" should be printed in bold type, and "III 94·5 4·7 2" in roman type.

Notes

Extraordinary General Meeting

An Extraordinary General Meeting of the Society of Dyers and Colourists was held in the rooms of the Society, 32–34 Piccadilly, Bradford, Yorks., on Wednesday, 14th June 1950, at 2.35 p.m., the President (Mr. F. Scholefield) being in the chair, and twenty-one other members of the Society being present.

The President read from the notice convening the meeting the purpose for which it had been called—

> To consider, and if thought fit approve, the following amendment to the Bye-laws, proposed by the Council—
>
> The addition to Bye-law 41, which reads as follows—
>
> "All general funds of the Society not required immediately for ordinary purposes, and all donations, bequests, and endowments, subject to any conditions thereof, may, with the authority of the Council, be invested in trustee securities and may, at the discretion of the Council, be sold or otherwise dealt with."
>
> of the following paragraph—
>
> *Provided that notwithstanding the foregoing provisions the Council shall have authority to invest a sum or sums not exceeding in the aggregate £5000 by deposit in Savings Banks for a period not extending beyond the 31st day of December 1955.*

The Honorary Secretary (Mr. J. Barritt) explained that the Council had in mind the desirability of making any further investments of the Society's funds in such a way as to avoid risk of capital loss, especially in view of the heavy outlay which will be necessary for the Second Edition of the *Colour Index*. However, a deposit in a Savings Bank was not regarded as a trustee security, and it was for this reason that the Council had unanimously recommended the proposed addition to Bye-law 41.

The President then formally moved the adoption of the proposed amendment to Bye-law 41; it was seconded by Professor J. B. Speakman, and carried unanimously.

The President concluded the meeting by thanking members for their attendance.

Proceedings of the Council

At a meeting of the Council, held at the offices of the Society, 32–34 Piccadilly, Bradford, on 10th May 1950, the proceedings included the following items of interest—

Investment of the Society's Funds— It was resolved unanimously that the President be requested to convene an Extraordinary General Meeting of the Society to consider an amendment to Bye-law 41 enabling a sum not exceeding £5000 to be deposited in Savings Bank accounts for a period not exceeding five years after 31st December 1950.

Committee Membership and External Representation— The review was continued of the membership of committees of the Society and its representation on external bodies. The resignation of Dr. C. M. Whittaker as the Society's representative on the Rayon Industry Committee of the British Standards Institution was accepted with regret.

Membership— Nine applications for ordinary membership were approved.

Meetings of Council and Committees— June

Council— 14th
Finance— 14th
Publications— 13th
Colour Index Editorial Panel— 19th
Diploma— 2nd
Summer School— 29th

Front Cover

The Society is greatly indebted to Mr. C. E. Kerr, late Head of the Department of Printing and Photographic Technology of the Manchester College of Technology, for the typographical design of the new front cover of the *Journal*. Mr. Kerr devoted much time and thought to the choice of a suitable fount and layout, and the Society would like to take this opportunity of expressing its gratitude for his very valuable assistance.

Perkin Centenary Committee

Council has set up a committee (p. 347) to consider what steps should be taken by the Society to celebrate the centenary of the discovery of Mauve by W. H. Perkin in 1856.

Fastness Tests Co-ordinating Committee

The work of the Society on fastness tests has been reorganised. In future the detailed work and technical discussion of the tests will be undertaken by small subcommittees, and the old Fastness Tests Committee has been replaced by a new Fastness Tests Co-ordinating Committee, the members of which are given on p. 346. Subcommittees have already been formed to deal with the tests for fastness to Alkaline Milling, Burnt Gas Fumes, Light, Perspiration, and Washing.

Deaths of Mr. C. A. Crook and Mr. T. F. Gorton

We regret to report the loss by death of Mr. C. A. Crook and Mr. T. F. Gorton, the latter a member

of the Moth and Dermestid Beetle Proofing Committee.

List of Council and Committees

In accordance with a decision of Council taken at its meeting on 11th January 1950 (J.S.D.C., **66**, 199 (Jan. 1950)) lists of officers, members of Council and committees, and representatives on external bodies are included in this issue of the *Journal* (pp. 345–348). It is intended that the publication of such lists in July instead of January will be continued in future years. Since elections to Council take place in March, and one of the first tasks of the new Council is to review membership of committees and representation on external bodies, the lists published in July will be up to date. Official notices and lists of medals and awards will continue to appear in the January issue.

Annual Meeting of Chairmen and Honorary Secretaries of Sections 1950

This meeting was held at the Queens Hotel, Leeds, on 1st April 1950, under the chairmanship of Mr. H. Jennison (Honorary Treasurer of the Society). Suggested subjects for lectures in the 1950–51 session were considered. Other topics discussed included publication of lectures in the *Journal* and the holding of colloquia.

Sectional Reports for the Session 1949-1950

HUDDERSFIELD SECTION

The 30th Annual Report of this Section again records a very successful session. As in previous years we have tried to give both the academic and the practical side in our lecture programme, and this year we have carried out an experiment by having a joint lecture with the West Riding Section, at Leeds University, which was very well supported by both Sections.

We have again had a joint meeting with the Huddersfield Section of the Royal Institute of Chemistry, and on this occasion we were favoured with a very excellent talk by Sir Wallace Akers on *Problems in the Production of Useful Power from Atomic Energy*. We also organised a discussion on *Uneven Dyeing and Other Problems*, when one of our own members, Mr. J. A. Wallwork, took part with Mr. H. Crook.

Our Annual Dinner, on 31st January 1950, was a very successful affair, and was attended by a record number of members and friends.

During this session we have formulated a revised set of Section Bye-laws, copies of which have been circulated to all members.

In conclusion, I should like to thank all the Officers of the Section, without whose splendid help this successful session could not have materialised.

H. TURNER
Honorary Secretary, Huddersfield Section

MANCHESTER SECTION

Eleven lectures were held during the session—nine in Manchester, one in Leek, and one in Preston. The high standard of the papers presented and the attendances experienced in the previous year were fully maintained; particularly so in the new venture at Preston, where the attendance was over 200. The Junior Branch continued its independent existence in spite of a low Junior membership— about 5% of the number of ordinary members. Attendances at the meetings were—

MANCHESTER

30th September 1949 — 125
Dye Transfer in the Steaming Process of Printing — H. A. Turner

21st October 1949 — 44
Some Relations, Economical and Technical, between the Pulp and Paper Trade and the Textile Trade — G. Ullmann (read by P. Bean)

17th November 1949 (Joint meeting with the Physical Society, the Society of Chemical Industry, and the Textile Institute) — 100
A New Approach to the Problem of the Structure of Cellulose and its Derivatives — F. Happey

16th December 1949 (Ladies' evening) — 75
Colour — Betty K. Battersby, J. M. Preston, and T. Vickerstaff

20th January 1950 — 79
Some Critical Factors affecting the Development of Brentogens in Textile Printing — R. Thornton

24th January 1950 (Joint meeting with the Textile Institute) — 105
The Setting of Nylon Fabrics — G. K. Mecklenburgh

17th February 1950 — 86
Targets for the Dyestuff Manufacturer — F. Farrington, N. Hamer, and G. M. Williams

24th March 1950 — 62
Recent Developments in Starch Chemistry in relation to some Technical Applications — J. Lolkema

21st April 1950 — 90
A Vat Dye Levelling Agent — R. W. Speke

LEEK

16th February 1950 (Joint meeting with the Leek Textile Society) — 28
The Dyeing of Narrow Fabrics — H. A. Thomas

PRESTON

15th March 1950 — 200+
Continuous Dyeing with Vat Colours — G. L. Boardman

Junior Branch

MANCHESTER

12th October 1949 — 16
Indigo Styles in Printing — F. Crompton

24th November 1949 — 40
Some Observations on the Dyeing and Finishing of Cellulose Acetate and Cellulose Acetate Mixture Fabrics — A. Mellor and H. C. Olpin

15th March 1950 — 35
Hats and Felts — D. Haigh

It is again a pleasure to thank the authors of papers for their contributions, and we are deeply grateful to Mr. F. Scholefield, the Manchester College of Technology, and the North-western Gas Board (Manchester Undertaking) for the facilities extended to us at ordinary and committee meetings.

Nine committee meetings were held during the session. In addition to the normal business of the Committee, perhaps the most concrete result of these was the submission to Council of a set of Section Rules. These were approved, and have been sent to all members.

We congratulate Mr. J. G. Evans on his appointment as Chief Chemist to the Bradford Dyers' Association Ltd. He was successively Honorary Secretary, Member of Committee, Vice-chairman, and Chairman of the Section, and was for many years of great assistance to us, particularly in matters relating to further education. We miss his services very much, and wish him well in his new work.

An informal dance, designed to appeal to the younger members of the Section in particular, was held at Belle Vue on 3rd March 1949. While it was generally agreed that this function was a social success, it was a financial failure, and accordingly a similar event could not be planned during the

winter of 1949–50. An appeal for donations to a Social Fund, which could cover any loss on a future function, has so far met with little response outside the Committee.

The Section continues its membership of the Manchester Federation of Scientific Societies, and has supported the 1949 Christmas Lecture for Young People.

The Knecht memorial prize was won by Mr. W. Clarke, who was a student at the Manchester College of Technology.

We have to record with regret the death of Dr. F. Townend, for three years Honorary Secretary of the Section.

The membership of the Section continues to increase, although the number of Junior members is only slightly greater than last year. The Committee hopes that senior members of the Section will do their utmost to encourage Juniors, with whom they come into contact, to consider membership of the Society and active participation in the Section's affairs.

	1948 (December 31st)	1950 (April 21st)
Members	515	560
Juniors	23	26
	538	586

A. S. FERN
Honorary Secretary, Manchester Section

MIDLANDS SECTION

We once more have pleasure in reporting a year of steady progress. New members showed a slight increase on last year, but owing to the migration of fifteen of our younger members to posts outside the Section, the net gain was not large. The figures are—

New members	42
Joined from other sections ...	10
Transferred to other sections	15
Resignation	1
Death	1
Net increase	35

This brings the total membership of the Section to 309.

Nine meetings were held, at which attendances were very satisfactory, averaging 76. The subjects of the lectures ranged from theory and review to more practical matters, and some very interesting discussions ensued. It is pleasing to record that one of the most successful meetings took the form of a presentation of a number of short papers on practical problems by local members. Fresh ground was broken by the first meeting to be held at Nuneaton, and an encouraging response has prompted us to arrange a return visit to the "Hatters" next session.

During November 1949, in conjunction with the Midlands Section of the Textile Institute, we sponsored a "Refresher Course for Technical Personnel" at the Leicester College of Technology. This extended over two week-ends, and comprised fifteen lectures by prominent members of both societies. It was highly successful, both from an educational and from a numerical standpoint. Indeed, the latter proved somewhat embarrassing, applications being nearly double the anticipated number.

"House full" notices went up once more at the Annual Section Dinner, at which we were happy to welcome the West Riding Chairman, his Secretary, and a number of visitors from other Sections. Once more our own members provided the entertainment, and a very enjoyable time ensued.

It was with great regret that lack of accommodation forced the Committee to turn down the invitation of the Council to act as host section for the 1950 Annual Meeting and Dinner of the Society. We are, however, most pleased to record that the invitation was repeated for 1951, and that accommodation was actually secured before the Leeds dinner!

Our Chairman, Mr. W. L. Langton, has been a regular attender at Council, while Mr. F. M. Stevenson, Vice-president, and Mr. W. Penn have ably supported him. A glance at the list of Committees of the Society appearing in this issue shows also a very representative number of Midlanders giving their time to the valuable work of the Society.

We record with regret the death of Mr. Tom Watson. Although not prominent in the Section, he was a very well known figure among Leicester master dyers.

We also regret to report the resignation of Mr. S. F. Bennett, who has left the industry. Mr. Bennett served the Section as Honorary Secretary from 1936 to 1946. While loath to lose him from the Committee, we wish him every success in the business he has just opened.

At the Annual Meeting of the Section, Messrs. Kershaw, McPherson, Olpin, and Tyler were re-elected to the Committee, while Mr. A. S. Cluley was chosen to take the place of Mr. Bennett. Subsequently, the Committee elected Mr. W. L. Langton as Chairman for a second year. Mr. McPherson retired from the Vice-chairmanship, his place being taken by Mr. Alan P. Kershaw (Chairman-elect).

The plans made by the Committee at its earlier meetings worked out so well during the session that it had to meet much less frequently, but its members continued to do valuable individual work in their local areas. With such practical help and personal friendship as exists in the Committee, it is a pleasure to serve the Society.

A. W. CARPENTER
Honorary Secretary, Midlands Section

NORTHERN IRELAND SECTION

There is nothing sensational to report regarding the 1949–50 session. It is, however, pleasing to record that a successful series of six lectures was delivered, and these were highly appreciated by members and visitors.

Membership has been maintained; and, although we had losses due to resignations, deaths, and transfers, it now stands at 105.

The following meetings took place—

1st September 1949
Opening Social Evening, during which were shown two sound films *Nobel began it* and *This is Colour*, kindly supplied and projected by Messrs. Imperial Chemical Industries Ltd

2nd October 1949 (Joint meeting with the Textile Institute)
Cloth Construction in relation to Textile Finishing H. W. Best-Gordon

3rd November 1949
A Comparison of Screen Printing Methods R. Thornton

4th December 1949
Colour in Nature N. McCraith

5th January 1950
The Dyeing of Nylon in Union with other Fibres J. G. Grundy

6th February 1950 (Joint meeting with the Society of Chemical Industry)
Colours in Food E. F. Eaton

7th March 1950
Contribution of Chemistry and Engineering to some Current Dyeing Problems R. G. Fargher

18th March 1950
Annual General Meeting and Dinner. The chief guests at dinner were Sir Graham Larmor and Mr. W. P. Walker.

It is with pleasure that we record our best thanks to the authors of all papers given, and to all those without whose sanction these would not have been possible.

JAMES PORTER
Honorary Secretary, Northern Ireland Section

WEST RIDING SECTION

Under the Chairmanship of Mr. J. M. Goodall, the Section can look back on another year of continued success.

Seven lectures have been held in Bradford (that to be given by Dr. R. L. Elliott being postponed owing to the General Election). These have all been well attended, and the concluding lecture, by Prof. N. Gralén of Sweden, has been commended as one of the most lucid we have had. Two lectures were held in Leeds, but the attendance was below expectations. The joint lecture with our Huddersfield colleagues was well attended, but this was a "special occasion".

Our two social functions, the "Smoker" and the Ladies' Evening, were again agreed to be outstanding successes.

The Committee have met on four occasions, the average attendance being twelve.

In conclusion, it is desired to commend the renewed activity of the Bradford Junior Branch, an innovation being the reading of competitive papers on one evening, at which members of the Section Committee were adjudicators. It is hoped that this will help to stimulate the activities of the Bradford Junior Branch.

At the Committee Meeting held after the Annual General Meeting on 23rd March 1950, the following officers were elected—

Chairman	... ...	Mr. E. A. Swift
Vice-chairman	... ...	Mr. C. O. Clark
Honorary Secretary	...	Mr. H. Foster

HAROLD FOSTER
Honorary Secretary, West Riding Section

Centenary of Professor J. J. Hummel

This year occurs the centenary of the birth of Professor J. J. Hummel, who played a prominent part in the growth of the Society. He was born at Clitheroe, Lancashire, on 26th February 1850, and a very full account of his scientific and other activities, including a list of his published papers, was given in the prize-winning essay by N. Walker, *The Life and Influence of Professor J. J. Hummel*, which was published in January 1939 (J.S.D.C., **55**, 14–30).

Japanese Dye Output

According to *The Dyer* (**103**, 427 (7th April 1950)), Japanese dye output showed a gradual increase from January to April 1949, and then declined, monthly production figures for 1949 up to July being 672, 660, 705, 721, 632, 564, and 480 tons. Present requirements are 300–400 tons.

Dye as Auxiliary Agent in Evaporation

In the extraction of potassium chloride from the Dead Sea, owing to the snow-white deposits of sodium chloride, only the infra-red radiation from the sun was being utilised to evaporate off the water. According to a report in the March 1950 issue of *Industrial and Engineering Chemistry* (p. 7A), a concentration of 0·0003% of Naphthol Green (*C.I.* 5) within a brine depth of 8 in. effected absorption of 90% of the visible and near infra-red portion of sunlight, thus leading to an increase in effective heat absorption of rather more than 03%. Three ancillary advantages resulting from the speeding up of evaporation were reduction in leakage from the pans, sharper demarcation between salt and carnallite, and reduction in contamination from air and soil owing to thicker carnallite deposits.

New Books and Publications

Dyeing with Coal-tar Dyestuffs

The Principles involved and the Methods employed

By C. M. Whittaker and C. C. Wilcock. 5th edition 1949. Pp. vii + 375, with 40 Fig. London: Baillière, Tindall & Cox. Price, cloth, 21s. 0d.

In a footnote to the preface of the new edition of *Dyeing with Coal-tar Dyestuffs*, the senior author bids farewell to his readers. Since 1918, when the book first appeared, a whole generation of members of this Society have had cause to be grateful to him, especially when it is remembered that for part of the period no other text-book on dyeing was available. Thousands of his past students, including the reviewer, will wish C. M. Whittaker a happy retirement.

Although Mr. Wilcock's style is less rugged than that of Dr. Whittaker, he is just as much a practical man, and the emphasis in this book is still very much on practice rather than on theory. This arrangement is satisfactory, both to the practical dyer and to the teacher of dyeing. By providing the necessary, but dull, practical details, the book enables the teacher to concentrate on the more agreeable task of providing a background in which the details are seen to fit together.

On comparing the present edition with the previous one, great changes are at once evident. The method of approach is no longer via the different classes of dyes. Instead, chapters devoted to individual fibres and groups of fibres begin with the vitally important preparatory processes, and

then proceed to the production of dyeings of different degrees of fastness, obtained by means of dyes of different types. This major revision brings the book into line with the modern approach to the subject.

Much new matter has been incorporated in the latest edition, although the number of pages remains almost unchanged. This has been achieved by increasing the number of words to the page and deleting or condensing matters of minor importance. The comparatively small, and very reasonable, increase in price does not make the book too expensive for students.

Among the more important additions are a chapter on water; and sections dealing with non-felting treatments; rayon cake dyeing and the classification of direct dyes; the dyeing of linen, alginate fibres, nylon, and Vinyon; the Abbot–Cox, pad–steam, and Multi-lap processes, and the Williams box. The dyeing of silk and acetate rayon are described in considerable detail in separate chapters. As might be expected, the rayon dyeing chapters are outstanding, considerable space being devoted to the preparation of rayon materials for dyeing, but cuprammonium rayon deserves more than six lines. A separate short chapter is devoted to theories of dyeing. In the final chapter, on the evaluation of dyes, many new fastness tests are described.

Although slightly marred by inadequate proof-reading, the latest edition of this book can be thoroughly recommended— to students and practical dyers alike. It is comprehensive, clearly written, and concise, as well as being attractively printed and reasonable in price. C. L. BIRD

The Cobbler

We are pleased to receive the second volume (1949–50) of this brightly produced record of the proceedings of the Huddersfield Local Centre of the Guild of Technical Dyers. The contents include the following articles of technical interest— *The Possibilities of Rayons in the Woollen Industry* (C. M. Whittaker), *The pH Control of Bulk Dyeings* (G. H. Lister), *From the Loom to the Public with emphasis on Cloth Analysis* (C. Mayland), *Faults in Wool Textiles* (F. F. Elsworth), *The Finishing of Woollen and Worsted Fabrics* (C. S. Whewell), and *Carpet and Rug Dyeing* (B. Kramrisch).

C. J. W. H.

Veredler-Jahrbuch Deutscher Färberkalender 1950

Edited by O. Mecheels. Pp. xviii + 213. Munich: Franz Eder Verlag. Price, DM 7.00.

This yearbook contains in a handy form information on the dyeing of various natural and synthetic fibres, but our readers will be most interested in the list of dyes and auxiliary products of the German and Swiss companies, as it gives a clear indication of the range of dyes available, with methods of application, recommended uses, and, in some cases, fastness figures. A. THOMSON

Reports on German Industry

Stockhausen & Cie., Krefeld Auxiliary Agents

FDX 786* (PB 74,955).

Microfilm of many pamphlets, published in German in 1940, on Stockhausen products. There are also analyses of many American and European auxiliary agents for the textile and leather trades. A number of methods for the chemical analysis of auxiliary agents are given, together with methods of evaluating the usefulness of such products. The preparation of several Stockhausen products is described, and there are a considerable number of laboratory and works reports on the production of auxiliary agents and products during 1931–45.

C. O. C.

Röhm & Haas G.m.b.H., Darmstadt Polymer and Enzyme Research

FDX 782* (PB 74,522; Microfilm I 290).

Microfilm of 300 research reports written in German during 1939–44. They deal with numerous aspects of the manufacture and use of polymers, particularly in textile finishing, and of the production and use of enzymes.

C. O. C.

Röhm & Haas G.m.b.H., Darmstadt Formaldehyde–, Acrolein–, Acrylic Acid–, and Methacrylic Acid–Urea Condensates and their Uses in Textile Finishing

FDX 792* (PB 74,547; Microfilm 1.295).

Microfilm of 186 research reports written in German during 1939–44. C. O. C.

I.G. Farbenindustrie A.-G., Wolfen Naphtol AS Dyes

FD 3182/48*.

Microfilm of two papers written in German in 1937. The first is entitled *Naphtol AS Dyes soluble in Organic Solvents* (6 pp.), and describes *inter alia* the production of Vulcan Fast Bordeaux BF, Pink CF, and Rubine BF. The second deals with work done in the Naphtol AS field during the previous year or so. C. O. C.

[I.G. Farbenindustrie A.-G.] Textile Series— Report No. 18 Supplementary Report on German Dyes

[Supplement to BIOS Misc. 20.] FD 2614/48* (PB 39,562).

Photocopy of a report by Allied investigators giving an account of the processes and materials used in making—

Hydron Olive GX

Immedial Black V extra and other brands; Black Brown GL extra, S extra, and V extra; Blue U 300 extra conc. and others; Brown BRD extra; Carbon L for paper; Catechu, various brands; Corinth B extra; Dark Green B; Direct Blue B extra and RL extra; Fast Dark Brown B extra; Green PT extra; Olive B, 3B, GN, and GR.

Immedialsols, various brands.

Indanthren Bordeaux RR, Brilliant Orange GR, Golden Yellow RK, Printing Black BL Suprafix paste, Printing Black F, Printing Brown 5R, Printing Olive GW Suprafix paste, Scarlet GG.

Printing Indocarbon CLN and JR Suprafix pdr.

Sulphur blacks and browns.

The manufacture of Glycinal is also described. C. O. C.

* Material available for inspection at, and photocopies available from, T.I.D.U., Board of Trade, Lacon House, Theobalds Road, London W.C.1, or (under PB No.) from Office of Technical Services, Department of Commerce, Washington D.C., U.S.A.

I.G. Farbenindustrie A.-G., Hoechst
Chlorinated Aliphatic Alcohols— Acetonitrile Trichloroacetamidines— Lævulic Acid— Pyrene Series

FD 2241/49* (part of PB 17,658).

Microfilm copy of 12 papers, written in German in 1936, including the following—

3-Bromopyrene and its Reaction Products
Benzoylpyrenic Acid and some Dyes from it
3:4-Benzpyrene
3(N):4-Pyridinopyrene and its Behaviour during Oxidation
Transition from the Pyrene to the Benzanthrone and Azabenzanthrone Series
Behaviour of Pyrene and its Halogeno Derivatives towards Aluminium Chloride
Substitution of Pyrenequinone
Action of Glycerol and Sulphuric Acid on Pyrene—Pyrene-peri-indenones
3:5:8:10-Tetra-aroylpyrene. C. O. C.

I.G. Farbenindustrie A.-G., Wolfen
Dibenzodioxan and its Derivatives
Polyoxydiarylenes— Acid Amide Chlorides
N-Substituted Naphthionic Acids— β-Methyl Naphthyl Ketone— Reactions with Symmetrical Dichloroacetone— Abietic Anhydride in Lacquers
1:6-Dinitro-2-naphthol— Di-(γ-chloro-β-hydroxypropyl)-arylamines and Derivatives
Slip-resistant Finish

FD 2243/49* (part of PB 17,658).

Microfilm of 10 papers, written in German in 1936, including one on the preparation of di-(γ-chloro-β-hydroxypropyl)-arylamines useful as coupling components for acetate rayon dyes and one on the production of a slip-resistant finishing agent from rosin and glycerosulphuric acid. C. O. C.

I.G. Farbenindustrie A.-G., Leverkusen
Arylides— Hydrogenation of Naphthalene Derivatives— *ar*-Tetralamines— Chrysene and Pyrene Series— Indolines— Carbazoles— Acridines etc.

FD 2232/49* (part of PB 17,658).

Microfilm of 28 papers written in German in 1935. They include the following—

Arylides from Methoxynitranilinesulphonic Acids
Nitration of 2-Naphthylamine-6-sulphonic Acid and its Acetyl Compound
1-Amino-7-naphthol-3-sulphonic Acid and Derivatives
p-*Carboxyphenyl-γ Acid and* p-*Carboxyphenyl-β Acid*
ar-*Tetralamines as Intermediates for Naphtol AS and Azo Dyes*
Hydroxyacenaphthenemonosulphonic Acids
9:10-Benzophenanthrene Series
Chrysene Series (two papers reviewing the entire field, including commercial uses)
New Indolines
New Indoles
Reciprocal Conversion of Bz-1-Amino- and Bz-1-Hydroxyquinolines and Acridines
Blue Dye for Acetate Rayon
Selenazole Series. C. O. C.

I.G. Farbenindustrie A.-G., Ludwigshafen
Vinyl Compounds— Nekals— Ramasits— Hexachloroethane— *p*-Alkylated Phenols— Aldehyde-*o*-hydroxycarboxylic Acid— Aromatic Mono- and Dicarboxylic Acids— Friedel–Crafts Synthesis

FD 2235/49* (part of PB 17,658).

Microfilm of 19 papers, written in German in 1936, among them being papers dealing with the manufacture of various Nekals and Ramasits. C. O. C.

I.G. Farbenindustrie A.-G., Uerdingen
Polymeric Olefins—α-Cyanosorbic Acid Butadiene— Hydrocarbons of High Molecular Weight— Substituted Succinic Acids

FD 2237/49* (part of PB 17,658).

Microfilm of 8 papers, written in German in 1936, dealing with the production of intermediates for auxiliary agents and dyes. C. O. C.

Ammoniakwerk Merseburg G.m.b.H., Leuna
"*iso*Butyl Oil" Alcohols— Ethyl Chloride— Phenols
*iso*Propyl Acetate— Ethylene Oxide

FD 2238/49* (part of PB 17,658).

Microfilm of 5 papers, written in German in 1936, one of which deals with the production of "*iso*butyl oil" alcohols and textile auxiliaries obtained from them. C. O. C.

I.G. Farbenindustrie A.-G., Leverkusen
Organic Fluorine Compounds— Reactions of Acid Chlorides with Ethylene Hydrocarbons—β-Halogenoketones— Phosphorous Esters of Higher Alcohols
Chloroaryl Compounds— Tanning Agents
Bucherer's 1:8-Aminonaphtholsulphurous Ester
Indoles— Hydroxycarbazoles— Naphtol AS

FD 2239/49* (part of PB 17,658).

Microfilm of 21 papers, written in German in 1936. Phosphorous esters of higher alcohols are useful as textile auxiliary agents. Several *N*-alkyl-3-hydroxycarbazole-2-carboxylic arylides yield dyes of poor fastness to light. C. O. C.

I.G. Farbenindustrie A.-G., Griesheim and Mainkur
o-Chlorotoluene— Aromatic Halogenopolynitro Compounds— Indane— 3-Chloro-4-aminophenyl Methyl Sulphone— Phenanthrene Derivatives
4-Hydroxynaphthostyryl— 2:2′-Diazoles
Trilon A

FD 2242/49* (part of PB 17,658).

Microfilm of 12 papers, written in German in 1936, dealing with the preparation of dye intermediates, including 3-chloro-4-aminophenyl methyl sulphone, one of the components of Celliton Fast Orange 5RF. There is a paper dealing with the softening of water by use of di- and triglycolamide acids, the former not being so powerful as the latter. Two methods of making Trilon A are given. C. O. C.

I.G. Farbenindustrie A.-G., Ludwigshafen
Effect of Acid Chlorides on Tetrahydrofuran
Production of Hexamethylenediamine from 1:4-Dichlorobutane— Tetrahydrofuran from 1:4-Butanediol

FD 2739/49* (part of PB 14,999).

Microfilm of 3 papers written in German in 1939. C. O. C.

I.G. Farbenindustrie A.-G., Ludwigshafen
Adsorption of Gases on Catalyst Carriers and Catalysts— Effect of γ-Butyrolactone on Ammonia and Monoamines— Dehydrogenation of Pyrrolidine and *N*-Substituted Pyrrolidines— Dihydrofuran and its Derivatives— Effect of Butyrolactone on Diamines

FD 2742/49* (part of PB 14,999).

Microfilm of 6 papers written in German in 1939. Dihydrofuran oxide forms with ammonia 3-amino-4-hydroxytetrahydrofuran, and with aniline 3-anilino-4-hydroxytetrahydrofuran, both of which can be used as components for diazo dyes for acetate rayon. C. O. C.

I.G. Farbenindustrie A.-G., Leverkusen
1-Amino-2-naphthyl Ethyl Ether— Nitration of Naphthol Esters— 3:3-Dichloro-oxindole and its Derivatives— Dealkylation of Pyridine Homologues— Aminopyrazoles— Methin and Dipyrazolonylphenylmethane Compounds as Mothproofing Agents— Cyanuric Chloride— Brown Coal Extracts

FD 2743/49* (part of PB 14,999).

Microfilm of 8 papers, written in German in 1939. One paper describes the preparation of various 3:3-dichloro-oxindole derivatives and their use in preparing intermediates for vat dyes for wool, particularly the 2-indole-3-indoleindigo type, which are red, brown, violet, blue, and grey, with excellent properties. Another paper describes work on polymethin and dipyrazolonylphenylmethane compounds as mothproofers. Very effective members of the latter series were found. As in the triphenylmethane series, hydroxy and halogen groups increase the mothproofing effect, whereas sulpho and amino groups reduce it. C. O. C.

* Material available for inspection at, and photocopies available from, T.I.D.U., Board of Trade, Lacon House, Theobalds Road, London W.C.1, or (under PB No.) from Office of Technical Services, Department of Commerce, Washington D.C., U.S.A.

I.G. Farbenindustrie A.-G., Leverkusen
Farina Preparations—Reactions with Acylated Ethyleneimines—Addition of Hydrocyanic Acid to Unsaturated Compounds—Side-reactions in the Sodium Hydroxide Melt of Benzenesulphonic Acid—Preparation of Diphenylamine Derivatives by using Metal Anilides and Aromatic Chlorine Compounds—Sulphones—Nitrophthalic Acid Derivatives—Substituted Phthalic Acids by Diene Synthesis

FD 2744/49* (part of PB 14,999).

Microfilm of 8 papers, written in German in 1939. One of them says that aromatic sulphones of all types are got in excellent yield when arylsulphonyl chlorides or arylenedisulphonyl chlorides are heated in presence of iron chloride catalysts with aromatic hydrocarbons or their oxides and sulphides. Another paper describes the preparation of carboxyaminobenzoylaminonaphtholsulphonic acids of especial interest as coupling components for Benzo Fast Copper dyes. C. O. C.

I.G. Farbenindustrie A.-G., Mainkur
Research Reports on Intermediates

FD 2745/49* (part of PB 14,999).

Microfilm of the following papers, written in German in 1939—

Substitution of Diazotisable Amino Groups by Aryl Radicals
Preparation of 1:5-Diaminonaphthalene-3:7-disulphonic Acid
Some New Acyl, Alkyl, and Aryl Derivatives of Aminonaphtholsulphonic Acids
Technical Production of Melamine
Production of Ethers of Thio-ammeline
Synthesis of Derivatives of Dihydrotriazine. C. O. C.

I.G. Farbenindustrie A.-G., Griesheim
Research Reports on Intermediates

FD 2746/49* (part of PB 14,999).

Microfilm of 5 papers, written in German in 1939. One of them dealt with a method, based on the Friedel–Crafts reaction, of introducing the *iso*propyl group into *o*-, *p*-, and *m*-dichlorobenzene and 1:2:4- and 1:2:3-trichlorobenzene to produce dye intermediates. Another paper deals with the preparation of nineteen substituted *o*-aminophenols intended as components for metalliferous azo dyes. C. O. C.

I.G. Farbenindustrie A.-G., Hoechst am Main
Research Reports on Intermediates, etc.

FD 2747/49* (part of PB 14,999).

Microfilm of 7 papers, written in German in 1939, viz.—

Progress in the Preparation of Blue Base F
2-Hydroxyanthracene-3-carboxylic Acids substituted in the 4 Position
New Fluorene and Fluorenone Derivatives
Derivatives of Ethyleneimine—
I—Reaction of Ethyleneimine with Hydrogen Sulphide
II—Reaction of Ethyleneimine with Thiols
III—Reaction of Ethyleneimine with Carboxyl and Sulphonyl Halides
Derivatives of Carbazole (48 are described)
Use of αβ-Unsaturated α-Halogenoaldehydes in preparing Benzanthrones
Derivatives of ββ′-Dihydroxy- and ββ′-Dichloro-diethyl Sulphide. C. O. C.

I.G. Farbenindustrie A.-G., Bitterfeld
Dyes as Ion-exchange Bases

FDX 788* (PB 73,967; Microfilm AA 118).

Among a large number of chemical research reports is one in which it is stated that some dyes have been found to have better ion-exchange properties than some of the Wofatits. Patent application was made for an ion-exchange base obtained by condensing certain dyes with *m*-phenylenediamine. C. O. C.

Gerresheimer Glashüttenwerke A.-G., Ettlingen
Leutz Process for making Artificial Fibres from Suitable Liquids by means of an Electric Field

FDX 767* (PB 82,159; Microfilm A 78).

A collection of documents, with drawings of plant, on the Leutz process for producing fibres from water-glass, and including a patent application of 1942. C. O. C.

* Material available for inspection at, and photocopies available from, T.I.D.U., Board of Trade, Lacon House, Theobalds Road, London W.C.1, or (under PB No.) from Office of Technical Services, Department of Commerce, Washington D.C., U.S.A.

Abstracts from British and Foreign Journals and Patents

(The Titles of Patents are abridged and modified)

I—PLANT; MACHINERY; BUILDINGS

Heat Transfer on Wet Surfaces. F. Rössler. *Naturwissenschaften*, **35**, 219, 220 (1948).

Size Reduction—Recent Improvements in Crushing and Grinding Machinery. R. V. Riley. *International Chem. Eng.*, **31**, 170–173 (April 1950).
A review with 28 references. C. O. C.

PATENTS

Continuous Formation of Carbon Black from an Endothermic Hydrocarbon Gas. C. Kaufmann, R. H. Hall, and Shawinigan Chemicals Ltd. *U.S.P.* 2,492,481.

Thread-storage, Thread-advancing Device for Use in Processing Freshly Spun Synthetic Threads. A. J. L. Moritz and American Enka Corpn. *U.S.P.* 2,492,055.

Nozzles for Drying Machines. J. Dungler. *B.P.* 636,130 and 636,154.

Drying Felt Hat Hoods. Taylor, Wordsworth & Co. Ltd. and F. Denham. *B.P.* 635,162.

Laundry Washing Machines. J. H. Banks. *B.P.* 635,258
Modification of *B.P.* 589,067 (cf. J.S.D.C., **63**, 356 (1947) and **64**, 287 (1948)). The outer cylinder is built up of several discontinuous segments providing spaced gaps extending the whole length of the cylinder. The strips between the outer and inner cylinders are disposed at or between these gaps so as to convert the annular space between the two cylinders into pockets of accurate section, communicating with the interior of the cage through the perforations in the inner cylinder, and with the exterior through the gaps or through perforations on the peripheral face of the segments or in the channel or other sections. C. O. C.

Tumbler Drying Machine. J. Haydock. *B.P.* 636,220.

Laundry Ironing Machine. Manlove Alliott & Co. Ltd. and W. A. Hastie. *B.P.* 636,437.

II—WATER AND EFFLUENTS

PATENTS

Softening Boiler Feed Water. C. Piccardo. *B.P.* 634,993.
The raw water is mixed with a solution of precipitation reagent, heating fluid, e.g. return boiler water, and softened water still containing suspended precipitation particles in a vertical cylindrical tank of height > diameter. Tangential jets ensure turbulence and efficient mixing. J. W. B.

Lime-Soda Softening Plant. J. Kruger. *B.P.* 635,269.
Plant is described which does not need large settling tanks and which does not tend to become clogged. C. O. C.

Lime-Soda Water Softening Plants and Effluent Treating Plants. Infilco Inc. *B.P.* 635,785.
A compact plant for the slurry type of treatment is described. C. O. C.

III—CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

The Alum Trade of East Yorkshire—I. A. Raistrick. *The Dalesman* (Lancaster), **12**, 23–25 (April 1950).

Most of the alum used by dyers in the 14th and 15th centuries was brought from Asia Minor by the Genoese. In 1462 it was discovered near Civita Vecchia in Italy, and the production and sales of Italian alum, which was much superior to that from Asia Minor, became a Papal monopoly. In 1595 alum shales were discovered near Gisborough in Yorkshire, and the alum manufactured there soon sufficed for the entire needs of British industry. C. O. C.

Water-soluble Cellulose Ethers as Emulsifying Agents. R. I. Morrison and B. Campbell. *J.S.C.I.*, **68**, 333–336 (Dec. 1949).

Methyl ethyl cellulose (I) has a wide range of use as an emulsifying agent, but tends to form foams; this can usually be avoided, however, by using some sodium carboxymethyl cellulose (II). Stable, non-creaming, non-foaming emulsions can generally be prepared by using in the aqueous phase 0·5% of I and 1·5% of high-viscosity II. In absence of II emulsions with I are stable over a wide pH range. I cannot be used to prepare emulsions above 40°C. II alone is an efficient stabiliser for mineral oil emulsions. It is best to use a high-viscosity grade, but if the amount used is $< 1\%$ there is a distinct reduction in stability. II alone is ineffective at low pH. Ease of emulsification is greater with I than with II, particularly at low concentrations, and this is reflected in their relative interfacial tensions. Methyl cellulose and methyl hydroxyethyl cellulose generally give coarser and less stable emulsions than I, but have a less marked tendency to produce foam. Improved emulsions with reduced foam are obtained by blending 1 part of these ethers with 3 parts of high-viscosity II. C. O. C.

Some Physical Chemical Properties of Aqueous Solutions of Soaps and Soapless Detergents. G. S. Hattiangdi, W. W. Walton, and J. I. Hoffman. *Bur. Stand. J. Res.*, **42**, 361–368 (April 1949).

The effects of concentration on surface tension, electrical conductance, pH, opacity, and foam formation are discussed in terms of micelle formation, and this is followed by a discussion of the relationship between micelles and detergent action. C. O. C.

Composition of Rosin Size Precipitate. D. Price. *Ind. Eng. Chem.*, **41**, 1274–1276 (June 1949).

Photochemistry of Rutile. W. A. Weyl and T. Förland. *Ind. Eng. Chem.*, **42**, 257–263 (Feb. 1950).

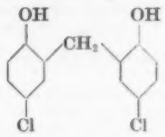
The colour, phototropy, and photoelectric oxidation phenomena of rutile are discussed on the basis of the crystal chemistry of defect structures. A sensitive test for atomic oxygen, which permits the detection of photo-oxidation within short exposure times, has been devised. The test is based on the oxidation of 4:4′:4″-hexamethyltriaminotriphenylmethane to the carbinol, which is the leuco base of Crystal Violet. The reagent is not oxidised by hydrogen peroxide. W. K. R.

Organic Compounds of Titanium—Tetraalkyl Orthotitanates, New Waterproofing Agents. R. J. Speer and D. R. Carmody. *Ind. Eng. Chem.*, **42**, 251–253 (Feb. 1950).

Tetraalkyl orthotitanates $Ti(O{\cdot}C_nH_{n+1})_4$, obtained by the action of titanium tetrachloride on alcohols in the presence of a condensing agent, are water-white, viscous liquids of high b.p. soluble in a wide range of organic solvents, e.g. aliphatic and aromatic hydrocarbons, alcohols, ethers, etc. They are very easily hydrolysed. They may be applied to all types of textiles from organic-solvent solution by impregnation, spraying, etc. and impart water-repellent properties. It is postulated that the water-repellency is due to hydrated titanium oxides formed by hydrolysis of the ester by moisture present in the fibres. W. K. R.

Fungicidal Activity of Bisphenols. P. B. Marsh, M. L. Butler, and B. S. Clark. *Ind. Eng. Chem.*, **41**, 2176–2184 (Oct. 1949).

Wide differences in fungicidal activity exist among the bisphenols tested. The most active compounds definitely tend to have certain common features and be free from others. The compound—



is typical of a group which are highly active. Activity is influenced by the following—(1) Number, type, and position of halogen atoms. Two Cl or Br atoms per mol. increase activity above that of the unhalogenated bisphenols, whereas too high a halogen content, especially of Br rather than Cl and/or particularly when occupying all four positions *ortho* to the phenolic OH, leads to low activity. (2) Unusually large molecular size imparts low activity. (3) Ether formation with the OH groups (but not necessarily esterification) causes very low potency. (4) Type of bisphenolic bridge—e.g. CH_2, S, CO, $CH(CH_3)$, $CH(C_6H_5)$, and CH:CH are compatible with high activity; SO, SO_2, and CO·CO are less desirable in this respect. (5) Substitution on the phenolic rings. The chlorothymol type of substitution brings about very low activity; certain other groups are not undesirable. C. O. C.

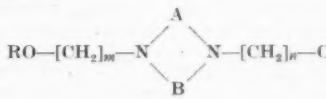
PATENTS

Alkarylsulphonate Detergents. Universal Oil Products Co. *B.P.* 635,303.

Removal of the unsulphonated and unsulphonatable hydrocarbons from either the neutralised sulphonate solution or the dried product considerably enhances the surface activity of the detergent. C. O. C.

Detergent. J. D. Malkemus and Colgate-Palmolive-Peet Co. *U.S.P.* 2,491,992.

Addition of 1–500% by weight of a compound of formula—



(R = alkyl or acyl of 5–23 C, A and B = ethylene or ethylene substituted by alkyl radicals of < 3 C, m and $n = 2$–5), e.g. a fatty acid monoester of 1:4-di-β-hydroxyethylpiperazine, to organic sulphates or sulphonates greatly improves both their foaming and detergent properties. C. O. C.

Cellulose Cyanoethyl Ethers. Courtaulds Ltd. and J. H. Macgregor. *B.P.* 636,020.

Water-sol. cyanoethyl ethers of cellulose are prepared by treating viscose with 0·5–1·2 mol. of acrylonitrile per anhydroglucose unit at not $> 40°$ C., and separating the water-insol. cellulose cyanoethyl ether, which is then dissolved or suspended in dil. aq. alkali soln., e.g. 0·7–1·2% aq. NaOH, and treated with a further 0·1–3·0 mol. of acrylonitrile per anhydroglucose unit originally present in the viscose. The product may be separated by neutralising with 10% HCl, dialysing against soft water, concentrating to a paste under reduced pressure, precipitating with alcohol, and filtering. They are useful as stabilising and emulsifying agents, sizes, and thickening agents for printing pastes, etc. J. W. B.

Organic Silicon Halides. Montclair Research Corpn. *B.P.* 635,194.

Substituted silicon halides are made in one step, without separately preparing the intermediate Grignard reagent, by treating a silicon halide or oxyhalide with a halogenohydrocarbon, such as an alkyl, aryl, or aralkyl halide, in the presence of metallic magnesium at a temperature at which refluxing takes place. They are useful in finishing compositions for textiles, e.g. in waterproofing and crease-resistant finishes. W. G. C.

Polyvinyl Acetate Emulsions. Shawinigan Resins Corpn. *B.P.* 634,216.

Stable emulsions of polyvinyl acetate containing $< 40\%$ polymer, which deposit films and coatings of high clarity, are prepared by polymerising vinyl acetate in aqueous emulsion at pH < 6, using as emulsifier the sodium salt of an organic sulphuric or sulphonic acid, e.g. sodium dodecylbenzenesulphonate, and as protective

colloid a hydrophilic colloid, e.g. gum arabic or polyvinyl alcohol. E. C.

Amine–Aldehyde Adhesives. I. F. Laucks Inc. and C. F. van Epps. *B.P.* 634,777.

An aqueous adhesive comprises wheat flour, an amine–aldehyde condensate, e.g. urea– or melamine–formaldehyde, and 1–6% by wt. on the flour of a water-sol. disulphite, e.g. sodium bisulphite. J. W. B.

Modified Furfuryl Alcohol Resins. Quaker Oats Co. *B.P.* 634,126.

Furfuryl alcohol (1 mol.) and ammonium thiocyanate (0·05–1·0 mol.) are heated under reflux, and an aldehyde (1 mol.), e.g. formaldehyde or furfural, is gradually added. The products are water-insol. thermosetting resins, suitable for use in coatings and in bonding laminates. E. C.

Polyvinylacetal Adhesives. S. Zweig and Milprint Inc. *U.S.P.* 2,492,512.

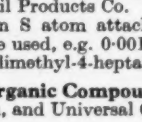
A thermoplastic coating composition, applicable when molten to cellulosic foils, paper, textiles, etc., comprises by weight 5–30% of a polyvinylacetal of 8–15% hydroxyl content, 25–85% of hydrogenated castor oil, and 2–25% of castor oil. The coated material is not tacky, but can be bonded to itself or other surfaces by means of heat and pressure. C. O. C.

Complex Salts of Stabilised Rosin Amine— Rot- and Mildewproofing Agents. G. L. Schertz and Hercules Powder Co. *U.S.P.* 2,492,939.

Complex metalammine salts having powerful fungicidal properties are obtained by treating complexogen metal salts with a stabilised rosin amine. Fabrics impregnated with small amounts of such salts are highly resistant to soil burial tests, the Cu, Zn, Cr, Hg, and Fe salts being particularly effective. Used in conjunction with chlorinated hydrocarbon flameproofing agents, they are effective stabilisers for the latter. The chromium chloride complex is useful also for tanning and preserving leather. C. O. C.

Pyrroles as Stabilisers for Halogenohydrocarbons. W. Klabunde and Du Pont. *U.S.P.* 2,492,048.

Halogenohydrocarbons, e.g. tri- or tetrachloroethylene, are stabilised by adding 0·001–1·0% by weight of a compound of formula—



(R^1 = H or Alk; R^2, R^3, R^4, and R^5 = H, Alk, or Hal), e.g. *N*-methylpyrrole. C. O. C.

Antioxidants for Organic Materials. R. B. Thompson and Universal Oil Products Co. *U.S.P.* 2,492,334.

Ketones having an S atom attached to the C atom β to the keto group are used, e.g. 0·001–0·5% by weight of 2:6-bisethylthio-2:6-dimethyl-4-heptanone. C. O. C.

Antioxidants for Organic Compounds. J. A. Chenicek, R. B. Thompson, and Universal Oil Products Co. *U.S.P.* 2,492,335.

Compounds of formula—

$$R^1{\cdot}CO{\cdot}CH_2{\cdot}CR^2R^3{\cdot}S{\cdot}X{\cdot}S{\cdot}CR^2R^3{\cdot}CH_2{\cdot}CO{\cdot}R^1$$

(R^1, R^2, R^3 = H, Alk, alkenyl, Ar, alkaryl, aralkyl, *cyclo*alkyl, or heterocyclic ring radicals; X = a hydrocarbon group in which the S atoms are attached to different C atoms) are used; e.g. 0·001–0·5% by weight of 5:8-dithiadodecane-2:11-dione is added to olive oil. *U.S.P.* 2,492,336.

A bis-γ-ketoalkyl sulphide is used, e.g. bis-γ-ketobutyl sulphide. C. O. C.

IV— RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

Mononitration of *p*-Xylene. K. A. Kobe and H. Levin. *Ind. Eng. Chem.*, **42**, 352–356 (Feb. 1950).

The effects of the following process variables in the nitration of *p*-xylene to mononitro-*p*-xylene have been investigated— temp. of nitration, time of addition of the mixed acids, ratio of nitric acid to *p*-xylene, and the dehydrating value of the sulphuric acid (D.V.S., defined as the wt. of sulphuric acid in the mixed acids divided by the total water present at the completion of nitration). A maximum yield of 90% was obtained by nitrating at 30° C. with a D.V.S. value of 3·0 and 11% excess nitric acid, the mixed acids being added in 30 min. No dealkylation was found to occur, and only small amounts of dinitro-*p*-xylene were formed. W. K. R.

Nitration of Nitro-*p*-Xylene. K. A. Kobe and T. B. Hudson. *Ind. Eng. Chem.*, **42**, 356–358 (Feb. 1950).

Nitro-*p*-xylene is readily nitrated to dinitro-*p*-xylene (60–80% 2:3- and 40–20% 2:6-dinitro-*p*-xylene) in 95% yield at 80°C. using mixed acids having a D.V.S. value of 8·0, and 10% excess nitric acid. W. K. R.

Bromination of Cresol. N. Ray. *J. Indian Chem. Soc.*, **26**, 587–590 (Dec. 1949).

A process of inhibiting the overbromination of the cresols is described, based on the fact that, when the volume of solution containing the cresol is so adjusted that the added reactants, potassium bromide and bromate, completely or nearly saturate the solution, then bromination is quantitative for nuclear substitution, and independent of temperature and concentration of bromine or acid added for its liberation. The mechanism of overbromination and of its inhibition is explained, and an easy and accurate method for the estimation of cresols by bromination is suggested. H. H. H.

Bromination of 6-Nitro-1-naphthylamine. H. H. Hodgson and R. E. Dean. *J.C.S.*, 822–823 (March 1950).

6-Nitro-1-naphthylamine dibrominates in chloroform solution at — 5°c. to give 2:4-dibromo-6-nitro-1-naphthylamine whatever the amount of bromine used. The monobromination previously reported by Hodgson and Turner (*J.C.S.*, 392 (1943)) using the calculated amount of bromine is found to give a mixture of 2:4-dibromo-6-nitro-1-naphthylamine and unchanged 6-nitro-1-naphthylamine. This result is in line with the nitration of toluene-*p*-sulphon-1-naphthalide, which always gives the dinitro compound (Hodgson and Walker, *J.C.S.*, 180 (1934)). H. H. H.

Some Derivatives of 5-Nitro-2-naphthylamine with a Note on its Preparation. H. H. Hodgson and R. E. Dean. *J.C.S.*, 820–822 (March 1950).

From a review of existing methods, it would appear that the most serviceable method for the preparation of 5-nitro-2-naphthylamine is the reduction of 1:6-dinitronaphthalene by alkaline hydrosulphide. 5-Nitro-*m*-nitrobenzenesulphon-2-naphthalide is nitrated further only by excess of nitric acid (sp. gr. 1·5) to give 1:5-dinitro-*m*-nitrobenzenesulphon-2-naphthalide, and this compound monobrominates probably to 3-bromo-1:5-dinitro-*m*-nitrobenzenesulphon-2-naphthalide. The 2-bromo-5-nitronaphthalene now described, together with the 1-bromo-7-nitronaphthalene (previous abstract), completes the set of bromonitronaphthalenes. H. H. H.

Some 1:7- and 1:2:7-Derivatives of Naphthalene. H. H. Hodgson and R. E. Dean. *J.C.S.*, 818–820 (March 1950).

7-Bromo-1- and 8-bromo-2-naphthylamine, 1-bromo-7- and 7-bromo-1-nitronaphthalene, 1:7-dibromonaphthalene, the 2-halogeno-1:7-dinitronaphthalenes, 7-nitronaphthalene-2:1-diazo-oxide, and the nitration of 7-nitro-*m*-nitrobenzenesulphon-2-naphthalide are described. Special conditions are necessary for the preparation of 7-nitronaphthalene-2:1-diazo-oxide. The nitration of 1:7-dinitro-*m*-nitrobenzenesulphon-2-naphthalide occurs in the naphthalene nucleus, as shown by hydrolysis of the nitration product to 1:5(?):7-trinitro-2-naphthylamine; the latter would not form a picrate, or deaminate readily. Similarly, 1:7-dinitro-2-naphthylamine is inert towards *m*-nitrobenzenesulphonyl chloride. H. H. H.

Nevile and Winther's Acid. G. Leandis. *Boll. Sci. Facoltà Chim. Ind. Univ. Bologna*, **6**, 42–44 (1948): *Chem. Abs.*, **44**, 1942 (10th March 1950).

By heating 1 mol. Na naphthionate and 4 mol. $NaHSO_3$ in an autoclave at 3 atm. for 10 hr. and using $Ca(OH)_2$ instead of NaOH for saponifying, the final yield of the acid reaches 82–83%. C. O. C.

Aminohydroxynaphthoic Acids. II—Attempted Synthesis of 7-Amino-4-hydroxy-2-naphthoic Acid ("Carboxy J-Acid") from 3-Amino-2-naphthoic Acid. W. F. Beech and N. Legg. *J.C.S.*, 961–966 (March 1950).

A large number of nitro and bromo derivatives of 3-amino-2-naphthoic acid are described in an attempt to find a suitable route to carboxy-J acid, but poor yields of two suitable intermediates, viz., 4:7-dinitro- and 4:7-dibromo-2-naphthoic acid, prevented their attempted conversion into this aminohydroxynaphthoic acid. H. H. H.

Synthesis of Cyanine Dyes. VI—A Further Note on the Synthesis of Lepidine. Y. Mizuno. *J. Pharm. Soc. Japan*, **69**, 126–129 (1949).

The Coupling Reaction. I—Coupling Power of Some Derivatives of Naphthalic Acid. H. Zollinger. *Helv. Chim. Acta*, **33**, 530–538 (May 1950).

The mechanism of the coupling reaction is explained on the basis of resonance theory, and the influence of the resonance reference structures is illustrated by means of the two coupling components, dimethyl-*o*-toluidine and β-naphthol. A remarkably small coupling power has been established for some naphthalic acid derivatives substituted by an auxochrome in the 3-position. The possible reaction behaviour and the colour of these naphthalic acid derivatives have been described, and also discussed from the standpoint of resonance theory. H. H. H.

The Coupling Reaction. II—Reactivity of the Hydroxyl Groups in 2:8-Dihydroxynaphthalene-6-sulphonic acid. H. Zollinger. *Helv. Chim. Acta*, **33**, 538–544 (May 1950).

The constitutions of the two isomeric esters obtained by reaction of 2:8-dihydroxynaphthalene-6-sulphonic acid with arylsulphonyl chlorides have been established. In general, the above dihydroxy compound couples with diazo compounds in the 1-position to form monoazo dyes, and its coupling behaviour is explained by the steric hindrance produced by the sulpho group. H. H. H.

Decomposition Reactions of the Aromatic Diazo-compounds. XII—Reaction between Diazo-compounds and Potassium Ferrocyanide. M. C. Ford, W. A. Waters, and H. T. Young. *J.C.S.*, 833–840 (March 1950).

Aromatic diazo compounds are found to react with potassium ferrocyanide solution to yield arylazodiaryls most smoothly at pH 4–5 in the presence of a sodium acetate buffer. Yields of about 20% were obtained with substituted aromatic amines $R{\cdot}C_6H_4{\cdot}NH_2$ when R = CH_3 or Cl, but with both the strongly *ortho–para*-directive substituent OCH_3 and the *meta*-directive substituent NO_2 the yield falls to below 0·5%. Degradative and synthetic reactions are described to establish the structures of the unsymmetrical arylazodiaryls obtained from *o*- and *p*-toluidine, *p*-chloroaniline, and α-naphthylamine. When R is in the *para* position to the nitrogen in the original amine, the reaction product is the 2-aryl derivative of a 4:4′-substituted azobenzene, and, when in the *ortho* position, a 4-aryl derivative of a 2:2′-substituted azobenzene is formed. Isomeric reaction products do not appear to be formed in appreciable amount. Possible reaction mechanisms are discussed. H. H. H.

Azobenzene. I—Vapour Pressure of *cis*- and *trans*-Azobenzene. N. F. H. Bright, T. Carson, and T. A. Dyson.

II—Infra-red Spectra of Slurries of *cis*- and *trans*-Azobenzene. T. Tetlow. *Research*, **3**, 185–188 (April 1950).

The fact that the two compounds show additive vapour pressures, their stoichiometrical identity as shown by microanalysis, and their different infra-red spectra all support the reality of the existence of the two materials as *cis* and *trans* isomers of azobenzene, and all conflict with Hodgson's view (*J.C.S.*, 1097 (1948)) that the *cis* isomer is a double compound of hydrazobenzene and azoxybenzene. C. O. C.

Nitration of *pp′*-Dichloroazobenzene. C. D. Houghton and W. A. Waters. *J.C.S.*, 1018–1019 (March 1950).

This nitration gives 4:4′-dichloro-2-nitroazoxybenzene, m.p. 134°C., and requires fuming nitric acid in glacial acetic acid; under less drastic conditions the *pp′*-dichloroazobenzene resists nitration. Whether nitration precedes oxidation or the reverse is not yet decided, but it is clear that both azo and azoxy groups have a very marked *ortho–para* orienting power. H. H. H.

Preparation of some Amino-1:4-Benzodioxans and Azo Dyes derived therefrom. P. M. Heertjes and L. J. Revallier. *Rec. Trav. chim.*, **69**, 262–270 (Feb. 1950).

Improved methods for the preparation of 6-nitro-1:4-benzodioxan, 6-amino-7-nitro-1:4-benzodioxan, and 6-amino-1:4-benzodioxansulphonic acid are described. Azo dyes derived therefrom when dyed on wool as acid dyes gave brilliant shades of generally good fastness to light and rubbing and moderate fastness to washing. Two azo pigments were also prepared from these compounds. H. K.

Intramolecular Nature of the Benzidine Rearrangement. G. J. Bloink and K. H. Pausacker. *J.C.S.*, 950–953 (March 1950).

From the rearrangement of the carboxy-substituted hydrazobenzenes, and from analogous experiments with benzeneazo-β-naphthol and 4-hydroxyazobenzene and their benzhydryl ethers, confirmation is claimed of the intramolecular nature of the benzidine rearrangement (cf. also Ingold and Kidd, *J.C.S.*, 984 (1933)). The authors report that, since their work was completed, Wheland and Schwartz (*J. Chem. Physics*, **17**, 425 (1949)) have obtained confirmatory evidence by a study of the rearrangement of an unsymmetrical hydrazobenzene, using ^{14}C as a radioactive tracer. H. H. H.

Electronic Structure, Colour, and Chemical Properties of Bisdiphenylene-ethylene and Bisdiphenylenebutadiene. B. Pullman and G. Berthier. *Compt. rend.*, **229**, 717–719 (1949): *Chem. Abs.*, **44**, 1803 (10th March 1950).

Whereas bisdiphenylene-ethylene is red, bisdiphenylene-butadiene is only orange. The hypsochromic effect of extension of conjugation in this case is explained on purely quantum-mechanical grounds without recourse to steric effects. C. O. C.

Preparation of Heterocyclic Ammonium Salt Dyes. VIII—Syntheses of 2-Amino-4-styrylquinoline Derivatives. IV—Specific Reaction of Primary Alcohols with 4-Alkoxyquinaldinium Salts. X—Styryl Dyes from Aromatic Heterocyclic Ammonium Salts. XI—Anil and Aniline Dyes from Aromatic Heterocyclic Salts. XII—Primary Studies on Syntheses of Aromatic Heterocyclic Ammonium Salts. VIII–XI—M. Katayanagi. XII—M. Katayanagi and S. Beppu. *J. Pharm. Soc. Japan*, **69**, 137–143, 237–248 (1949).

Cyanine Dyes—Thiacyanine Dyes containing Thiocarbamide Groups. N. F. Turitsyna and I. I. Lerkser. *Doklady Akad. Nauk S.S.S.R.*, **66**, 871–874 (1949): *Chem. Abs.*, **44**, 1839 (10th March 1950).

An account of the preparation and properties of a number of 3:3′-diethyl-6:6′-bis(alkylthiocarbamido)-thiacarbocyanine dyes. C. O. C.

New Method of Preparation of Iminocyanines. A. van Dormael and J. Libeer. *Science et Ind. phot.*, **20**, 451–454 (1949): *Chem. Abs.*, **44**, 1839 (10th March 1950).

s-Iminocarbocyanines are prepared by condensing quaternary salts of 2-methylbenziminazoles in nitrobenzene solution in presence of ethyl orthoformate. C. O. C.

Heightening of Sensitivity of Infra-red Photographic Plates by Organic Pigments. O. Makaki and K. Yamamoto. *Rept. Japan. Assocn. Advancement Sci.*, **16**, 342–344 (1942).

Liver Tumours in Mice injected with Commercial Food Dyes. A. H. M. Kirby and P. R. Peacock. *Glasgow Med. J.*, **30**, 364–372 (1949): *Chem. Abs.*, **44**, 2631 (25th March 1950).

In stock mice benzeneazo-β-naphthol is a hepatotropic carcinogen when injected subcutaneously. "Oil Yellow HA" gave suggestive but not conclusive results. C. O. C.

Natural Indian Dyes and their Application. A. N. Gulali. *Indian Textile J.*, **60**, 223–229 (Dec. 1949).

A review of the literature, there being 30 references. C. O. C.

Flavonols from the Bark of *Melicope ternata*. III— Synthesis of Quercetin 3:3′-Dimethyl Ether, Quercetin 3:7:3′-Trimethyl Ether, Quercetin 3:5:7:3′-Tetramethyl Ether, Ternatin, and Related Benzyl Ethers. L. H. Briggs and R. H. Locker. *J.C.S.*, 864–867 (March 1950).

The compounds listed in the title have been synthesised by a combination of Allan and Robinson's flavonol synthesis (*J.C.S.*, **125**, 2192 (1924)) and Seshadri's nuclear oxidation by potassium persulphate (*Proc. Indian Acad. Sci.*, **28 A**, 1 (1948)). The appropriate free phenolic groups were protected by formation of their benzyl ethers. H. H. H.

Colouring Matters similar to Methylpteridine Red from various Methylpteridines and from Pteridine. P. Karrer, R. Schwyzer, and B. J. R. Nicolaus. *Helv. Chim. Acta*, **33**, 557–559 (May 1950).

By heating mixtures of 8- or 9-methylpteridine with 8:9-dimethylpteridine or pteridine in 20% sulphuric acid in presence of air, it was found that red pigments were formed only when one molecule contained a methyl group and the other was unsubstituted in the 9-position respectively, e.g. 8:9-dimethylpteridine with 8-methylpteridine or with pteridine, and 9-methylpteridine with pteridine. The mixture of 8-methylpteridine and pteridine gives one or several substances having a green colour. H. H. H.

White Pigments. T. Hoog. *Verfkroniek*, **22**, 238–240 (1949): *Chem. Abs.*, **44**, 2765 (25th March 1950).

A comparative review of the most important properties of white lead, basic silicate–white lead, basic lead sulphate, ZnO, $ZnSO_4$, lithopone, TiO_2, $PbSiO_3$, and antimony oxide. C. O. C.

Flushing in the Preparation of Pigment Pastes. H. P. Teunissen. *Verfkroniek*, **22**, 233–237 (1949): *Chem. Abs.*, **44**, 2766 (25th March 1950).

A discussion, with 14 references, of the different factors decisive in successful flushing of pigments. C. O. C.

Ultramarine— an Inorganic Preparation. R. G. Woodbridge. *J. Chem. Education*, **26**, 552 (1949): *Chem. Abs.*, **44**, 1766 (10th March 1950).

Ultramarine (1–3 g.) is prepared by finely grinding kaolin (100 parts), Na_2CO_3(100), charcoal (12), and S(60), and tightly packing the mixture into a small porcelain crucible. The crucible is covered, and then heated to at least a bright red for 1·5 hr., the cover is removed, and after firing for another 0·5 hr. and cooling, the ultramarine is easily separated from the colourless material. C. O. C.

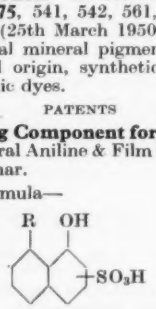
Colours in Cosmetics. K. Rothemann. *Seifen-Öle-Fette-Wachse*, **75**, 541, 542, 561, 562 (1949): *Chem. Abs.*, **44**, 2708 (25th March 1950).

Review on natural mineral pigments, plant pigments, pigments of animal origin, synthetic mineral pigments, and synthetic organic dyes. C. O. C.

PATENTS

Cyan Azo Coupling Component for Diazotype Colour Process. General Aniline & Film Corpn., S. C. Slifkin, and T. J. Trojnar. *B.P.* 635,120.

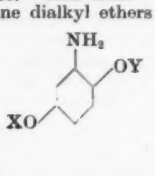
Compounds of formula—



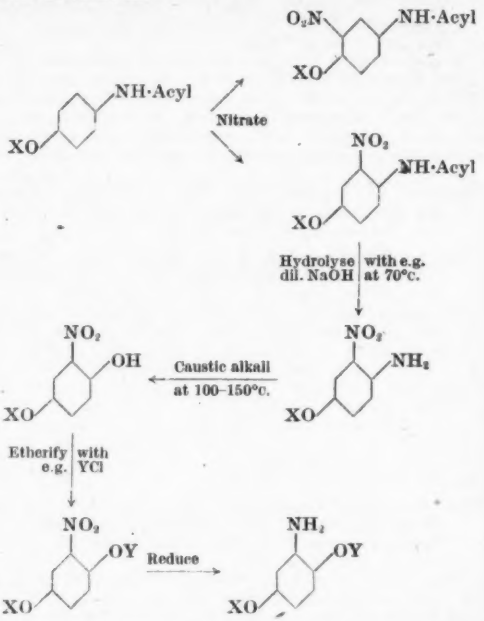
(R = hydroxyl, amino, acylamino, alkylamino, or arylamino), e.g. 1:8-dihydroxynaphthalene-4-sulphonic acid, when used in conjunction with light-sensitive diazo compounds derived from an *N*-substituted *p*-phenylenediamine, e.g. the zinc chloride double salt of the diazonium chloride from *p*-diethylamino-*o*-phenetidine, yield greenish-blue images of high intensity when exposed through a red separation positive. C. O. C.

Aminohydroquinone Dialkyl Ethers— Intermediates for Azoic Dyes. Ciba Ltd. *B.P.* 634,390.

Aminohydroquinone dialkyl ethers of the type—



(X and Y are different alkyl groups) are made by the series of reactions—



Thus, starting with acetyl-*p*-anisidine, and using ethyl chloride at the etherification stage, 2-aminohydroquinone 1-ethyl 4-methyl ether is obtained. The arylide prepared by condensing this amine with 2:3-hydroxynaphthoic acid couples in substance or on the fibre with e.g. diazotised 2:5-dichloroaniline to give fast browns. E. S.

5-Acyloxypyrazoleamidoaldehyde Acetals of Vinyl Alcohol Polymers useful as Colour Formers for Azomethine Dyes. Du Pont. *B.P.* 635,294.

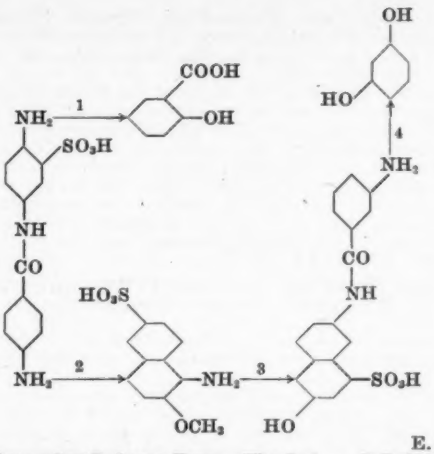
A vinyl alcohol polymer is condensed with a 5-acyloxypyrazole containing an amidoaldehyde group $-R^1{\cdot}Y{\cdot}NH{\cdot}R^2{\cdot}CHO$ (R^1 and R^2 = bivalent organic radicals; Y = CO or SO_2) in the 1- or 3-position, or with a lower acetal of such an aldehyde. The aldehyde must be free from substituents which react with aldehyde or ketone groups and must have an H atom attached to the carbon atom in the 4-position. C. O. C.

Chromable *o*-Hydroxymonoazo Dyes. Sandoz Ltd. *B.P.* 634,488.

Metallisable *o*-hydroxymonoazo dyes are made by esterifying or etherifying the OH group *para* to the azo group in metal complexes of the monoazo dyes *o*-aminophenol or *o*-aminonaphthol→resorcinol or β-resorcylic acid, and removing the metal from the reaction product by means of acids or salts. Thus the copper complex of the monoazo compound 4-chloro-2-aminophenol-6-sulphonic acid→resorcinol is esterified with toluene-*p*-sulphonyl chloride. Copper is removed from the molecule by treatment with HCl, to yield a product giving brownish yellows on wool, converted to bordeaux by afterchroming. E. S.

Green Substantive Tetrakisazo Dyes. J. R. Geigy S.A. *B.P.* 634,429.

Bright green substantive dyes which may be after-treated on the fibre with formaldehyde or diazotised *p*-nitroaniline have the general formula A←B→C→D→E (A = an *o*-hydroxybenzoic acid; B = a mono-(*m*- or *p*-aminobenzoyl)-*p*-phenylenediamine; C = a 2-alkoxy-1-naphthylamine; D = a 1-(*m*- or *p*-aminobenzoylamino)-8-naphtholsulphonic acid, or other *p*-aminobenzoylamino-naphtholsulphonic acid, coupling in *ortho* position to the OH group, whose acylamino and OH groups are in positions allowing the formation of binuclear naphthaquinones; E = a *m*-dihydroxy-, *m*-diamino-, or *m*-aminohydroxy compound of the benzene series; the final dye contains 3 or 4 sulpho groups). An example is the dye—



E. S.

Substantive Polyazo Dyes. Ciba Ltd. *B.P.* 636,006.

Substantive polyazo dyes are made by coupling tetrazotised 3:3′-dihydroxy-4:4′-diaminodiphenyl first with 1 mol. of a coupling component containing a sulpho group (particularly a naphtholsulphonic acid, but an azo compound may be used), and then with a coupling component free from sulpho groups (especially β-naphthol), this second coupling being accomplished in the presence of > 25% pyridine on the weight of the coupling mixture. Thus, if the first coupling component is 2-naphthol-6-sulphonic acid, and the second is β-naphthol, the product dyes cellulose fibres violet by the single-bath or two-bath aftercoppering process. E. S.

Introducing Amino Groups into Aromatic Compounds. J. S. F. Turksi. *B.P.* 626,661.

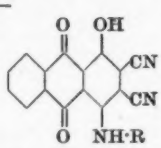
An aromatic compound is heated at <101°c. with hydroxylamine or one of its salts in sulphuric acid in presence of a metallic salt to give a nuclear amino derivative. Thus, all parts being by weight, anthraquinone (20·8) is heated for 10 hr. at 100°c. with 93% sulphuric acid (200), hydroxylamine sulphate (8·5), and vanadyl sulphate (0·7). 22·9% of anthraquinone is recovered unchanged, while a yield of 31·3% of β-aminoanthraquinone is obtained. R. K. F.

α-Aminoanthraquinones. M. Scalera, D. R. Eberhart, and American Cyanamid Co. *U.S.P.* 2,486,210.

α-Chloro- and α-bromo-anthraquinones are heated at 150–200°c. in an inert solvent, e.g. nitrobenzene, with phthalimide in presence of copper powder or a copper salt, anhydrous sodium acetate, and pyridine or quinoline bases. The resulting phthalimido derivative is hydrolysed in sulphuric acid to the corresponding amino compound. R. K. F.

Reddish-blue Anthraquinone Acetate Rayon Dyes fast to Acid Fading. British Celanese Ltd. *B.P.* 614,969.

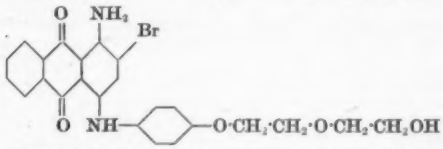
Dyes of formula—



(R = alkyl, *cyclo*alkyl, aryl, or aralkyl) dye organic derivatives of cellulose reddish blues of unusual resistance to acid fading. They are obtained by treating a 1-hydroxy-2-sulpho-4-aminoanthraquinone, whose 4-amino group carries an alkyl, *cyclo*alkyl, aryl, or aralkyl group as a substituent, with aqueous NaCN or KCN at 75–90°c. until an anthraquinone derivative containing the cyano groups is produced. C. O. C.

Anthraquinone Derivatives—Dyes for Cellulose Esters and Nylon. J. B. Dickey, A. Loria, E. B. Towne, and Eastman Kodak Co. *U.S.P.* 2,487,045.

A 2:4-dihalogeno-1-amino(or substituted amino)-anthraquinone is condensed with a derivative of aniline, nuclear-substituted with $-O\cdot CH_2\cdot CH(OH)\cdot CH_2OH$ or $[O\cdot D]_n\cdot O\cdot R$ (D = ethylene, propylene, or trimethylene; R = H, CH_3, or C_2H_5; and n = 1–3), to give blue dyes, fast to light and gas fumes, for cellulose acetate and nylon. Thus 1-amino-2:4-dibromoanthraquinone and *p*-aminophenyl β′-hydroxy-β-ethoxyethyl ether are heated at 120–150°c. for 24 hr. in Methyl Carbitol in presence of potassium acetate and copper acetate. The dye—



is separated by pouring into water and is crystallised from ethanol. R. K. F.

1-Amino-4-hydroxy-5-chloroanthraquinone. J. Deinet, F. B. Stilmar, and Du Pont. *U.S.P.* 2,487,110.

1-Amino-4:5-dichloroanthraquinone is heated in conc. sulphuric acid containing boric acid for 5 hr. at 150–155°c. After diluting to 70% H_2SO_4 the sulphate of 1-amino-4-hydroxy-5-chloroanthraquinone is filtered off and hydrolysed by washing free from acid. Alternatively, the 1-nitro-4:5-dichloro compound is used, when iron powder is added during the treatment at 150–155°c. R. K. F.

1-Amino-4-(nitro-2′-hydroxy)phenylaminoanthraquinone-2-sulphonic Acids—Chromable Acid Dyes. C. G. Verdery, C. G. Vogt, and General Aniline & Film Corpn. *U.S.P.* 2,485,121.

Neutral-dyeing green to black acid (referred to throughout the original as "vat") dyes are made by condensing 1-amino-4-bromoanthraquinone-2-sulphonic acid with a nitrated *o*-aminophenol, which may carry other groups, e.g. SO_3H, Hal, etc. Thus 1-amino-4-bromoanthraquinone-2-sulphonic acid is refluxed under nitrogen for 5 hr. with an aqueous solution of 6-nitro-2-aminophenol-4-sulphonic acid containing sodium bicarbonate, cuprous bromide, and sodium sulphite. The product is isolated by filtering hot and acidifying the cooled filtrate. R. K. F.

α-Di*cyclo*hexylylaminoanthraquinone Derivatives. J. Ogilvie and Allied Chemical & Dye Corpn. *U.S.P.* 2,485,764.

Leuco-1:4-dihydroxy(or diamino)anthraquinones are condensed with a di*cyclo*hexylylamine to give blue colouring matters suitable for oils, waxes, lacquers, and plastics. Thus leuco-quinizarin is refluxed for 16 hr. in alcohol with 2-amino-1-*cyclo*hexyl*cyclo*hexane. After cooling and filtering, the resulting leuco derivative is oxidised with alcoholic nitrobenzene containing alkali. R. K. F.

Metal-free Phthalocyanines. W. L. Rintelman and Du Pont. *U.S.P.* 2,485,167.

A phthalonitrile is heated in an inert organic solvent in presence of <20% of its weight of a primary or secondary amine, e.g. *cyclo*hexylamine or piperidine, to give a metal-free phthalocyanine. Thus phthalonitrile is heated at 200–210°c. for 12–14 hr. in trichlorobenzene containing *cyclo*hexylamine. After cooling, the resulting phthalocyanine is filtered off and freed from solvent by drying or steam-distilling. *U.S.P.* 2,485,168.

Similar products are prepared at lower temperatures (160–180°c.) by replacing the primary or secondary amine by a mixture of piperidine (or a homologue), ethylene glycol, and an alkali-metal carbonate. R. K. F.

Phthalocyanine Sulphur Dyes. R. L. Mayhew and General Aniline & Film Corpn. *U.S.P.* 2,484,300.

In reducing copper phthalocyaninetetrasulphonyl chloride to give sulphur dyes, smaller quantities of iron replace the zinc usually used. Thus the mixture resulting from reaction of copper phthalocyanine with chlorosulphonic acid is reduced by adding hydrochloric acid and iron borings (twice the weight of phthalocyanine) at 40°c. After heating further at 75–90°c. the product is filtered. R. K. F.

Phthalocyanine Pigments. S. A. Loukomsky and American Cyanamid Co. *U.S.P.* 2,486,304.

Phthalocyanine pigments free from the undesirable property of increasing in particle size when in contact with organic liquids are prepared by mixing or grinding

together in a suitable apparatus, e.g. a Werner–Pfleiderer mixer, an unground phthalocyanine, a grinding aid, e.g. salt or calcium carbonate, and an organic liquid, e.g. xylene, the latter being added gradually as mixing proceeds. R. K. F.

Photosensitising Dyes. H. D. Edwards, J. D. Kendall, and Ilford Ltd. *B.P.* 624,027.

Azamerocyanine Dyes—Photographic Sensitisers. General Aniline & Film Corpn. and T. R. Thompson. *B.P.* 636,403.

Carbon Black. Phillips Petroleum Co. *B.P.* 635,898.

The helical-flame carbon black process is adapted to producing special types of carbon black in reactors of large diameter, thus solving the "multi-apparatus" problem associated with the production of channel blacks. C. O. C.

Iron Oxide Pigments. P. J. Atkin, J. B. Peel, and I.C.I. Ltd. *B.P.* 635,177.

Red iron oxide pigments of exceptional brightness are obtained by oxidising with air a hot alkaline aqueous suspension of ferrous carbonate containing a small proportion of a magnesium compound. C. O. C.

Continuous Formation of Carbon Black from an Endothermic Hydrocarbon Gas. C. Kaufmann, R. H. Hall, and Shawinigan Chemicals Ltd. (I, p. 382.)

Reducing Agents from Alkali Sulphides suitable for mixing with Sulphur Dyes. Ciba Ltd. (VIII, p. 391.)

Light Absorption and Fastness of Dyes. S. Sakurai. (XIV, p. 396.)

V—PAINTS; ENAMELS; INKS

Factors affecting the Colour of Titanium Enamels. C. Millar. *Ind. Finishing*, **2**, 451, 452, 454, 456–460 (1950): *Chem. Abs.*, **44**, 2723 (25th March 1950).

The usual causes for off-colour white enamels are Fe and Cr; Ga has a similar effect. Creaminess may be caused by alteration in the crystalline structure of TiO_2: if in rutile form, the enamel will be cream; if in anatase form, a cold neutral white. C. O. C.

VI—FIBRES; YARNS; FABRICS

Fibres. R. S. Casey and C. S. Grove. *Ind. Eng. Chem.*, **41**, 2119–2121 (Oct. 1949).

A review of fibre production and uses in 1948; there are 107 references. C. O. C.

Development of the Textile Industry in Canton Glarus. R. Freuler. *Textil-Rund.*, **5**, 123–133 (April 1950).

Iklé Textile Collection in the St. Gallen Industries and Trades Museum. P. Quensel. *Textil-Rund.*, **5**, 149–152 (April 1950).

Special Dyeing of Cotton on the Seed gives Visual Evidence of Changes during Fibre Development. C. F. Goldthwait, H. O. Smith, and F. T. Roberts. *Text. Research J.*, **20**, 100–104 (Feb. 1950).

By differentially dyeing cotton on the seed it has been shown visually that the drying of cotton fibres for the first time, i.e. in the cotton field, greatly affects their dyeing properties. The relationship between the colour of the dyed fibre produced by the use of a dye mixture in the differential dyeing technique and the cellulose structure is discussed. P. C.

Examination of Bast Fibre from *Calotropis gigantea*. B. Biswas and D. Y. Athawale. *Proc. Natl. Acad. Sci., India*, **17 B**, (2), 76–82 (1947): *Chem. Abs.*, **44**, 2247 (10th March 1950).

A sample of the fibre from S. India, with strands 18–24 in. long, was cut and passed through a 40-mesh screen. The fibres had an average thickness of 16·29μ. Staining tests showed close similarity to flax, but provide an easy means of distinguishing between the two fibres. Microscopic examination revealed other characteristics differentiating the two fibres, especially in the transverse section. The fibres contain 80·6% cellulose, of which 93·72% is α-cellulose. The lignin content is 2·21%. C. O. C.

Measuring Water Evaporation through Different Textile Fibres. R. Signer and M. Roth. *Makromol. Chem.*, **3**, 281–285 (1949): *Chem. Abs.*, **44**, 2248 (10th March 1950).

One end of a fibre wick is placed in a weighed flask of water, the other end is in contact with air of known temperature and R.H. The rate of evaporation of the water is determined by weighing the flask. Rates of evaporation through viscose rayon, cotton, wool, casein fibre (Al process), and glass fibre are in the ratios 3·5 : 2·5 : 1·1 : 1·1 : 1·0 : 2·0. That the rate of evaporation is not dependent on the water absorption of the fibre is shown by the corresponding absorption values of 77, 36, 24, 37, 31, and 4%. C. O. C.

Internal Membranes in Animal Fibres. H. Zahn and H. Haselmann. *Melliand Textilber.*, **31**, 225–230 (April 1950).

A report, illustrated by phase-contrast and bright-field photomicrographs, of experiments on the structure of animal fibres. Smooth bands have been isolated from horsehair by mechanical means and are shown to lie below the outer scales. They exhibit double refraction and a fibrillary structure, and therefore can be regarded as covering the spindle cell layer. The intermediate membranes obtained by heating human hair in 2N-NaOH at ordinary temp. are shown to be bands from the outermost cortical cells. The components of sheep's wool which are insol. in 2N-NaOH at ordinary temp. are shown to consist of scale covering and cortex skin. B. K.

Sorption of Acids by Wool. R. Donovan and P. Larose. *Canadian J. Res.*, **27 B**, 879–889 (Dec. 1949).

The amount of acid sorbed by wool from solutions of sulphuric acid of four different strengths (0·0101–0·0505 M.) containing sodium sulphate up to 0·16 M. has been determined. Within these limits the presence of the salt has little effect on the quantity of acid sorbed. The results obtained may be explained on the basis of the Peters and Speakman application of the Donnan equilibrium but not by the theory of Gilbert and Rideal. It is shown that various data for the absorption of H_2SO_4 and of HCl by wool fit the Langmuir absorption isotherm equation and give values for maximum combining capacity in good agreement with those estimated in other ways. W. K. R.

Relaxation of Stress in Wool Fibres. S. M. Katz and A. V. Tobolsky. *Text. Research J.*, **20**, 87–94 (Feb. 1950); *Text. Manuf.*, **76**, 238–242 (May 1950).

The relaxation of stress at constant extension of Columbia wool fibres in water and in sodium bisulphite solutions has been studied. Qualitatively, the behaviour in water is similar to that observed for Cotswold fibres, an increase in temperature causing an increased relaxation rate. The magnitude of this increase diminishes as the initial extension is increased. There are, however, some points of difference between Columbia wool and human hair in relaxation properties. The relaxation rate of wool is greater in sodium bisulphite solution than in water. When wool fibres are first held extended in water until the rate of relaxation is low, and then sodium bisulphite added to the water, there is a marked increase in relaxation rate due to the chemical action of the reagent. The rate of stress decay depends upon concentration at low bisulphite concentration, but becomes independent of concentration above 0·05 M. Degree of extension has no effect, whilst temperature increases relaxation rate. Solutions of neutral salts cause extended and relaxed fibres to undergo an additional relaxation. P. C.

Structure of Silk Fibroin. B. Drucker and S. G. Smith. *Nature*, **165**, 196–197 (4th Feb. 1950).

When a solution of silk fibroin in cupri-ethylenediamine is neutralised and dialysed through a Cellophane sac against running water an aqueous solution of fibroin is obtained, which according to Coleman and Howitt exists in two forms, a denatured part with an extended chain configuration, and a renatured form with the molecules folded around "proline hinges". By means of paper partition chromatography the chemical identity of the two forms has been established, and it has also been shown that both forms have an amino-acid composition identical with fibroin itself. Experiments on the disposition and mol. wt. of the constituent amino acids enable a reasonably complete structure of the folded renatured fibroin to be elucidated. H. K.

Examination of Rayon Cross Sections with the Electron Microscope in conjunction with Supplementary Light-microscopic Observations. P. H. Hermans. *Text. Research J.*, **20**, 105–108 (Feb. 1950).

Sections of viscose fibres of 1 μ. or less have been examined in an electron microscope. A photograph is shown in which the presence of small voids in a rather thick cortical layer of the fibre is evident. The thickness of this layer corresponds to about that of the fibre skin as revealed by staining techniques, and the voids probably produce the phenomenon of "milkiness". Various light-microscope photographs of fibre cross-sections under different conditions of illumination are shown, and serve to demonstrate the complex internal structure of the viscose fibre. P. C.

Theory of Ester Resonance in Cellulose Compounds. S. Sönnerskog. *Svensk Papperstidning*, **53**, 185–187 (15th April 1950).

It is claimed that the ageing of alkali cellulose, the sensitivity of oxycelluloses to soda lye, and the breakdown of nitrocellulose by the action of strong bases can in general all be explained theoretically by assuming the hydrogen atom linked to the first carbon atom in the glucose units to possess a high degree of mobility. Migration of this proton would cause an ester resonance, resulting in hydrolysis of glucosidic ether linkages. S. V. S.

Partial Acetylation of Cotton Cellulose by Keten. C. Hamalainen and J. D. Reid. *Ind. Eng. Chem.*, **41**, 1018–1021 (May 1949).

Linters and cotton sewing thread have been acetylated with keten. Treatment involves preswelling with water, removal of excess water by extraction, suspension of the cotton in an inert solvent (preferably ether) containing a catalyst (preferably perchloric acid), and treatment with keten as prepared by pyrolysis of acetone. Samples containing up to 17% acetyl retained their fibrous structure with only slight degradation. The keten acetylation was accompanied by an objectionable polymerisation of keten, which produced a yellow to dark brown coloration of the sample. The colour could be removed by hot alcohol. Although the emphasis was on the reaction of water-activated, solvent-dehydrated cellulose with keten, some experiments were tried in which cotton was swollen with acetic acid before introduction of keten. Acetylation was probably due to the acetic anhydride formed. M. E. W.

Heat Stability of Cellulose Acetate. E. F. Evans and L. F. McBurney. *Ind. Eng. Chem.*, **41**, 1260–1264 (June 1949).

Interaction of Cellulose with Alkaline Solutions of Metal Hydroxides. [Determination of Cobalt.] A. Pakshver, M. Arkhipov, and B. Geller. *J. Appl. Chem.* (*U.S.S.R.*), **23**, 181–191 (Feb. 1950).

A study has been made of the behaviour of cellulose (cuprammonium rayon staple fibre) when immersed in the following solutions— aq. NaOH; solutions of Cu, Zn, and Co hydroxides in aq. NaOH; solutions of Cu, Zn, Co, and Ni hydroxides in aq. ammonia; and the foregoing with additions of urea and pyridine. Measurements were made of the absorption of the metal hydroxide by cellulose, the composition of the soln. being such that a negligible amount of cellulose was dissolved. Measurements were made also of the solubility of cellulose in solutions of suitable composition. It was found that the complex metal hydroxides were absorbed by cellulose more strongly from their solutions in aq. NaOH than from ammoniacal soln. In NaOH soln. the degree of absorption increased in the order— $Zn(OH)_2 < Cu(OH)_2$; and in ammoniacal soln. in the order— $Zn(OH)_2 < Ni(OH)_2 < Cu(OH)_2$. The solubility of cellulose in ammoniacal solutions of the metal hydroxides was in the same order— $Zn(OH)_2 < Co(OH)_2 < Ni(OH)_2 < Cu(OH)_2$. Its solubility in solutions of the hydroxides of copper and cobalt in aq. NaOH was less than in the straight aq. NaOH, although, in the analogous absorption experiments, the uptake of copper hydroxide was very high. Additions of urea and pyridine did not affect the solubility of cellulose in aq. NaOH, but in all other cases they resulted in an increased solubility. The lower the solubility of cellulose in the complex metal hydroxide soln., the greater was the effect of the added substance. The results confirm that the solubility of cellulose in such solutions depends firstly on the formation of a complex compound of the metal hydroxide with caustic soda or ammonia, and secondly on the ability of the metal hydroxide to split away from this compound and unite with the hydroxyl groups of cellulose. The results show also that the formation of this compound with cellulose does not in itself lead to increased solubility.

In the course of this work a new rapid method for the determination of cobalt was evolved— 25 ml. of the soln., containing a cobaltous salt, is placed in a tall beaker, and 20 ml. of 10% NaOH soln. added, followed by 20 ml. of 100-vol. H_2O_2. Vigorous reaction proceeds with the formation of cobaltic hydroxide. The soln. is diluted to 100 ml., boiled for 15 min., and cooled. Potassium iodide (25 g.) is added, followed by conc. H_2SO_4 up to 5 ml. in excess of neutrality. The iodine liberated is titrated with thiosulphate. A. E. S.

Processing of Nylon in U.S.A. F. Schläppi. *Textil-Rund.*, **5**, 135–141 (April), 201 (May 1950).

Topics discussed are the setting of nylon by saturated steam, preheated steam, and heated calenders; scouring, bleaching, and dyeing; comparative tensile strength of nylon and other textiles; effects of steaming and of exposure to light, heat, and sulphuric acid on the tensile strength of nylon; identification of nylon in mixtures. B. K.

Influence of Molecular Structure on the Swelling of Textile Fibres. J. M. Preston. *J. Textile Inst.*, **41**, T 126 (March 1950).

The high axial swelling and relatively small transverse swelling of undrawn nylon are incompatible with the assumption that it is a homogeneous, randomly oriented fibre, but may be explained if the nylon fibres possess a "skin" structure. A photomicrograph of undrawn nylon fibres between crossed polarisers indicates that a thin doubly refracting skin is present, the thickness of which is approx. one-tenth of the radius of the fibre. In this skin, the double refraction is positive in the tangential direction, which implies a preferred orientation of the molecules parallel to the surface. A. S. F.

Chemical Changes in Wool resulting from Wear and Dry Cleaning. E. L. Phelps, L. O. Lund, and H. W. Norton. *Amer. Dyestuff Rep.*, **39**, 177–180, 202 (20th March 1950).

Trousers manufactured from 12-, 14-, and 16-oz. all-wool serge were worn for experimental periods of 1500, 3000, and 4500 hr., each garment being dry-cleaned 5 times during each 1500-hr. period. Alkali solubility and the percentage of nitrogen, sulphur, and ash were selected as measures of the chemical change resulting from wear and/or dry cleaning of the garments, and the results of these experiments are tabulated. H. K.

PATENTS

Viscose Preparation. M. Golben and American Viscose Corpn. *U.S.P.* 2,492,421.

Controlling the Ageing of Xanthates. J. P. Hollihan, S. A. Moss, and American Viscose Corpn. *U.S.P.* 2,492,428.

Preventing the Blocking of Spinnerets. North American Rayon Corpn. *B.P.* 634,868.

The addition of a 0·0001–0·05% of a surface-active polymerised alkylene oxide to the spinning bath or the viscose solution prevents the incrustation of the spinneret, e.g. Wax 4000 (Carbide & Carbon Chemicals Corpn.), a polymerised ethylene oxide having a degree of polymerisation of 91. W. G. C.

Crinkled or Potentially Crinkled Regenerated Cellulosic Filaments from Viscose. P. H. Schlosser, R. L. Mitchell, and Rayonier Inc. *U.S.P.* 2,491,937 (with K. R. Gray) *U.S.P.* 2,491,938.

Desulphurising High-denier Viscose Rayon. Courtaulds Ltd. and R. M. Lodge. *B.P.* 635,113.

Cakes of high-denier viscose rayon relatively free from carbon disulphide are produced by collecting the yarn in a spinning box having a number of additional holes to allow the carbon disulphide to escape, and rotating the box for a further period, e.g. 1 hr. W. G. C.

Cellulose Esters. G. A. Richter and American Viscose Corpn. *U.S.P.* 2,492,442 *U.S.P.* 2,492,443.

Wet Protein Preparations. R. Campbell, H. Taylor, A. J. Baillie, and I.C.I. Ltd. *B.P.* 635,309.

Wet protein preparations with improved keeping properties, comprising undissolved purified protein in aqueous slurries, suspensions, or creams, are prepared by passing sulphur dioxide through the alkaline protein extract until the isoelectric pH is reached, and washing with water. The dilute suspension is thickened by centrifuging to give e.g. a 25% slurry in water, to which is added 20% by wt. of protein of 10% sodium sulphite solution brought to the same pH with sulphurous acid. J. W. B.

Hardening Protein Fibres. N.V. Onderzoekingsinstituut "Research". *B.P.* 634,812.

The stability of casein fibres in hot acid dyebaths is improved by treating in a solution of the acid condensate of resorcinol and formaldehyde. W. G. C.

Polyamides. Wingfoot Corpn. *B.P.* 634,172.

Non-linear polyamides which are thermoplastic and capable of forming strong fibres and coating compositions are made by heating an amino acid or a mixture of amino acids having a single amino group and a single carboxyl group separated by ≥ 4 atoms, or an amide-forming derivative, with a selected polycarboxylic acid, e.g. 1 mol. of 3:3:5:5:3′:3′:5′:5′-octa-β-carboxyethyl-4:4′-diketodi-*cyclo*hexyl and 100–5000 mol. of ε-caprolactam. W. G. C.

Hydrolysed Ethylene Interpolymers. I.C.I. Ltd. *B.P.* 634,140.

Products which can be made into fibres and films are obtained by treating an interpolymer of ethylene and a vinyl ester until 80–95% of the ester groups are hydrolysed. W. G. C.

Plasticisers for Polyvinyl Chloride. Compagnie Française de Raffinage. *B.P.* 636,400.

Hydrocarbons containing only one benzene nucleus, this nucleus being substituted by one or more aliphatic chains of > 9 C each and the nucleus and/or the chains being chlorinated, e.g. the product obtained by condensing benzene with chlorinated aliphatic gas oil, are used. C. O. C.

Plasticised Vinyl Chloride Copolymers. C. W. Gayler and American Viscose Corpn. *U.S.P.* 2,492,419.

Vinyl chloride–acrylonitrile copolymers are plasticised with 2–20% by weight of thymol, *iso*thymol, orcinol, methylenedisalicylic acid, 2-methyl-3:5-di*iso*propylphenol, mixtures of alkylated phenols, *p*-chlorophenol, 2:4-dichlorophenol, or 1:3-dihydroxy-4-chlorobenzene. Besides their plasticising action these compounds also serve as heat-stabilising agents. Filaments from the plasticised product have increased hardness, toughness, and tensile strength.

U.S.P. 2,492,420.

Monohydric alcohols containing 5–9 C, e.g. *cyclo*hexanol or benzyl alcohol, are used. C. O. C.

Synthetic Preparations from Starch. D. Horsak. *B.P.* 635,274.

Synthetic films or fibres are prepared by mixing starch or starch-containing material with water and a softener, e.g. 30% by wt. of glycerol or $CaCl_2$, gelatinising into a pasty mass, and removing water to produce a pseudo-thermoplastic composition, which is shaped under heat and pressure. J. W. B.

Stabilisation of Periodate-oxidised Cotton. R. E. Reeves and F. F. Darby. (VII, this page.)

Degradation of Cellulose as revealed Microscopically. C. W. Hock. (X, p. 392.)

Transparent Polyamides. Du Pont. (XIII, p. 394.)

VII— DESIZING; SCOURING; CARBONISING; BLEACHING

Preferential Wetting of Cotton Fabrics. I. Reich and F. D. Snell. *Ind. Eng. Chem.*, **41**, 2797–2800 (Dec. 1949).

A two-phase wetting technique is described involving displacement of oil from the fibres and measurement of the sinking time to pass through the interface. Molecularly dehydrated phosphates show sinking times of a few seconds; other salts commonly used as builders show times > 60 sec. This effect is associated with a multivalent negative ion. Mathematical prediction that addition of synthetic detergents to molecularly dehydrated phosphates would increase the sinking time is confirmed. These results correlate with unusually good detergency of the synthetic detergents on cotton when the detergents are highly built with molecularly dehydrated phosphates. The results are attributed to effects at the fibre surface rather than at the oil–water interface. C. O. C.

Bleaching Goods for Dyeing and Finishing in the Continuous Open-width Peroxide System. J. L. Moore. *Amer. Dyestuff Rep.*, **38**, P 497–P 499, P 504 (27th June 1949).

A description of modern American practice. C. O. C.

Stabilisation of Periodate-oxidised Cotton. R. E. Reeves and F. F. Darby. *Text. Research J.*, **20**, 172–174 (March 1950).

When cotton is oxidised with periodate, the fibre is sensitive to subsequent treatment with aqueous alkali. Attempts have been made to counter this instability by interposing a suitable aftertreatment to the oxidation process, and two reagents, chlorous acid and ethereal diazomethane, have been evaluated for this purpose, using a cotton sewing thread. Treatment with 70 parts of a solution containing 20 g. sodium chlorite, 100 ml. glacial acetic acid, and 500 ml. water for 24 hr. at room temp., followed by rinsing and air drying, was an effective stabilising process. Alternatively, protection was afforded by treatment for 1 week at 5°C. in 30 parts of a neutral ethereal 0·32 M. diazomethane solution. At low levels of oxidation there was actually an increase in strength after exposure to sodium carbonate of the oxidised, stabilised cottons, whilst at high levels of oxidation good reduction in alkali-solubility was obtained. P. C.

Processing of Nylon in U.S.A. F. Schläppi. (VI, p. 389.)

Photodegradation of Dyes on Matt Acetate. Influence of Bleaching on Degradation. J. Pinte and Mlle. Goujet. (XIV, p. 396.)

VIII— DYEING

Applications of the Automatic Tristimulus Integrator to Textile Mill Practice. H. R. Davidson and I. H. Godlove. *Amer. Dyestuff Rep.*, **39**, P 78–P 84 (6th Feb. 1950).

The application of colour measurement to control of wool dyeing and the evaluation of the results of fastness tests using the combined G.A.F. Librascope Automatic Tristumulus Integrator and General Electric Recording Spectrophotometer are briefly described. H. K.

Contribution of Solvation to the Stability of Anthraquinone Vat Dye Suspensions. D. P. Graham and A. F. Benning. *J. Phys. Colloid Sci.*, **53**, 846–860 (1949): *J. Textile Inst.*, **41**, A 73 (Feb. 1950).

A general expression relating the electrokinetic (ζ) potential to ionic concentration at the point of incipient flocculation of a hydrophobic suspension is used to evaluate the contribution of solvation to the stability of aqueous suspensions of anthraquinone vat dyes (particle sizes 0·02–0·2 μ.). The function selected for this purpose was the ratio ("solvation ratio") of the ionic concentration of an electrolyte experimentally found to effect incipient flocculation of a suspension, to that calculated to produce the same effect upon an unsolvated suspension at the same ζ-potential. The structural formulæ of the dyes used are listed. Results tabulated for the solvation of 14 dyes in the presence of various electrolytes show not only the wide variation in degree of solvation of different dyes, but also the effect of lyotropy, and it is indicated that only uni-univalent electrolytes (e.g. NaCl) should be used to measure the degree of solvation of a suspension. The stability–solvation results were related to migration tendencies by passing strips of white cloth through 0·3% aqueous suspensions of the individual dyes, drying the fabrics from one side, and evaluating the resulting migration in terms of reflectance. As the solvation ratio increases, the severity of the observed migration also increases, indicating that the latter is quite closely associated with solvation of the suspension. M. E. W.

Adsorption of Dyes by Textile Fibres. J. L. L. Chave, *Afinidad*, **25**, 498–503 (1948): *Brit. Abs.*, **B II**, 783 (1949): *J. Textile Inst.*, **40**, A 20 (Jan. 1950).

Adsorption of dyes by textile fibres is considered in relation to Freundlich's equation and adsorption isotherms,

and some results are tabulated and graphed, including values of x (amount adsorbed) derived from that equation, both calculated and found, for different concentrations. The fibres tested included viscose rayon, and more particularly Viscosilla H-3 and H-7, and the dye chiefly used was Durazol Grey NS. The effect of electrolytes (NaCl and Na_2CO_3) in the bath was also studied; it was found that the flocculating effect was due not only to neutralisation through electrolytic dissociation, but also to a certain extent to reduced concentration of dye. M. E. W.

Adsorption Phenomena in the Textile Industry. J. Cegarra. *Anales Invest. textil* (Barcelona), **1**, 29–40, 99, 100 (1949): *Chem. Abs.*, **44**, 2247 (10th March 1950).

Fixation of dye from a solution containing 25×10^{-5} g. Dark Green BN per ml. by cotton at 80°c. reached equilibrium in 1 hr., but Chlorantine Orange 2GL took 4 hr. Equilibrium (i.e. 1 hr.) fixations of Dark Green BN as g. dye fixed per kg. cotton, determined with 5 g. of cotton in 500 ml. of solution containing 2, 4, 8, 16, 20, and 24×10^{-5} g. dye per ml. were— at 100°c. 0·96, 1·30, 1·71, 3·30, 7·55, and 8·60; at 60°c. 1·38, 1·40, 1·99, 6·19, 10, and 10·28; at 20°c. 0·61, 1·27, 1·38, 1·80, 4·45, and 5·30; at 60°c., with addition of 17×10^{-3} g. Cl electrolyte per ml., 3·00, 5·86, 11·68, 13·86, and 14·97. The dye fixation curve obtained at 60°c. with addition of electrolyte follows the Freundlich adsorption equation closely. All the dye was absorbed by silk from a solution containing 66×10^{-3} g. of Brilliant Green per ml. at 20°c. The implications of these findings for dyeing practice are critically discussed. C. O. C.

Short Process for the Dyeing of Wool with Indigosols. Durand & Huguenin A.-G. *Textil-Rund.*, **5**, 141–144 (April 1950).

Dyeing is carried out for 35–45 min. at 85°c. with Glauber's salt and an anionic auxiliary product such as Indigosol Soap W or Surfactol DH, and is followed by development with sulphuric acid, ammonium thiocyanate, Indigosol Soap W, and potassium dichromate for 15 min. at 85°c. B. K.

PATENTS

Reducing Agents from Alkali Sulphides suitable for mixing with Sulphur Dyes. Ciba Ltd. *B.P.* 636,399.

Reducing agents especially suitable for use with sulphur dyes are obtained by treating a degradation product of a natural carbohydrate of high mol. wt. or a carbohydrate of low mol. wt. in conc. aqueous solution at not $>$ 108°c. with an alkali sulphide, the product being dried at not $>$ 108°c. They are suitable for mixing with dry or wet sulphur dyes or their leuco compounds to yield dye compositions directly soluble in water. Dyebaths prepared by use of these agents work at a higher pH than those prepared with sodium sulphide, and in addition the salt content of the bath may be reduced. C. O. C.

Natural Indian Dyes and their Application. A. N. Gulali. (IV, p. 385.)

Special Dyeing of Cotton on the Seed gives Visual Evidence of Changes during Fibre Development. C. F. Goldthwait, H. O. Smith, and F. T. Roberts. (VI, p. 388.)

Processing of Nylon in U.S.A. F. Schläppi. (VI, p. 389.)

IX—PRINTING

PATENT

Printing on Transparent Sheeting. Shellmar Products Corpn. *B.P.* 636,271.

Regenerated cellulose film, etc. is printed on one side with a quick-drying ink, and then the unprinted side is passed close to a source of radiant heat. Suitable apparatus is described. C. O. C.

Natural Indian Dyes and their Application. A. N. Gulali. (IV, p. 385.)

X—SIZING AND FINISHING

Rise of the Wool-textile Industry [in West Yorkshire]. A. Raistrick. *Bradford Textile Soc. J.*, 21–24 (1948–49).

A brief account of developments in the 17th and 18th centuries. C. O. C.

The First Cropping-shears. R. Patterson. *Bradford Textile Soc. J.*, 29, 30 (1948–49).

A brief history of cropping-shears, the use of which has been traced back to Roman times in both Britain and Italy. C. O. C.

Application of Infra-red Drying to Textiles. J. Schneider. *Melliand-Textilber.*, **31**, 284–286 (April 1950).

Infra-red drying is stated to increase production in Sanforising by 25% and in wool carbonising by 10%, and to facilitate continuous machine printing of textiles. Figures for infra-red drying of textiles are as high as 450 m./min. Limited application is claimed for wool under present-day methods of production. B. K.

Recrystallisation of Regenerated Cellulose upon Mercerisation. P. H. Hermans, D. Vermaas, and A. Weidinger. *Nature*, **165**, 238 (11th Feb. 1950).

It has been shown by X-ray examination that treatment of viscose rayon fibres with 18% NaOH solution at room temp. for 10 min. causes an increase in crystallinity from an initial value of 40% to 50–55%. An explanation is offered for the similar increase in crystallinity which occurs on boiling viscose rayon in acid. W. K. R.

Velanation of Cellulosic Materials. P. V. Afanasey and S. E. Bresler. *Colloid J. U.S.S.R.*, **10**, 249–258 (1948): *Brit. Abs.*, **B II**, 1026 (1949): *J. Textile Inst.*, **41**, A 129 (March 1950).

Theoretical considerations are advanced for the mechanism of "velanation", and on these bases certain polyfunctional Velan analogues were synthesised and used for the treatment of cellulose and other materials. Thus, viscose threads were soaked for 10 hr. in aqueous solutions of the reagents, removed, and heated for 20 min. at 120°c. in a thermostat, washed in water, and dried at room temperature. Separate experiments established that addition of an equivalent amount of sodium acetate to the solutions of the reagents completely destroyed the "velanation" action. The mechanical properties of the treated materials were studied, and results are given for "velanation" by the compound $O([CH_2]_3 \cdot O \cdot CH_2 \cdot C_3H_5NCl)_2$, the properties changing sharply. The compound $CH_3 \cdot CH_2 \cdot O \cdot CH_2 \cdot C_3H_5NCl$ acts as a plasticiser, i.e. it increases the irreversible deformation of the threads. Experiments on filter paper are also reported; "velanation" increases the strength of the paper about 1000-fold. The methods used in general are distinguished from the usual methods of "velanation" in that the conditions are milder. The results obtained are in close agreement with those of other authors. M. E. W.

Creasing and Creaseproofing of Textiles. D. D. Gagliardi and I. J. Gruntfest. *Text. Research J.*, **20**, 180–188 (March 1950).

The strains imposed on filaments in the bending or creasing of multifilament fabrics are considered in relation to their stress–strain curves, with particular reference to viscose. By chemical modification with formaldehyde or formaldehyde resins, the ability of fibres and hence of fabrics to recover from creasing is improved. The importance of maintaining the multifilament character of the fabric when applying creaseproofing agents is stressed. Resins that diffuse into the fibre impart a high degree of crease resistance, in contrast to those that are merely deposited on the surface, thus cementing fibres together. The properties of viscose and cotton fibres after the application of a variety of creaseproofing treatments are described. Under normal conditions of treatment, the reduction in various properties such as strength, tear resistance, and abrasion resistance, resulting from such treatment, is a natural consequence of the decrease in fibre extensibility. The need for improvements in creaseproofing agents is stressed. P. C.

Water-impermeable, Water-vapour-permeable Coated Fabrics— Development of a Waterproof Coated Fabric which transmits Body Perspiration. G. E. Martin, H. S. Sell, and B. W. Habeck. *Text. Research J.*, **20**, 123–132 (Feb. 1950).

A coated fabric based on the combination of a solid pigment and rubber composition has been developed which is waterproof and yet permeable to water vapour. It possesses good flexibility, flex- and abrasion-resistance, and resistance to ageing and to washing and/or dry-cleaning. Field tests have shown it to be a useful fabric, and further work is in progress. P. C.

Microbiological Deterioration of Cellulose during the First 72 hours of Attack. E. Abrams. *Text. Research J.*, **20**, 71–86 (Feb. 1950).

The changes which occur in cellulosic fibres due to the action of five cellulolytic moulds during the first 72 hr. of attack have been studied by observing the change in strength due to mould growth, the microscopical appearance and chemical resistance of damaged fibres, the extent of growth of the moulds on modified celluloses and on sugars, the decomposition products arising from growth, and the effects of enzymes of *Chætomium globosum* on several forms of cellulose. Microbiological damage as evidenced by loss in strength occurs much sooner than is usually suspected, before the mould growth can be detected by the unaided eye. Alkali-resistance tests on mildewed fibres showed that serious damage occurs at relatively early stages, e.g. after 12 hr. incubation, and that attack is highly localised. As the attack proceeds, the cellulose becomes soluble in decreasing concentrations of alkali, and finally in water. It was shown that *C. globosum* is capable of utilising a variety of sugars and such compounds as cellobiose octa-acetate and glucose penta-acetate, but no growth is obtained on cellulose acetate or partly acetylated cellulose. P. C.

Degradation of Cellulose as revealed Microscopically. C. W. Hock. *Text. Research J.*, **20**, 141–151 (March 1950).

The degradation of cellulose by chemical, physical, and biological agencies has been followed by optical and electron-microscopical methods. Many beautiful photographs, including some electron-photomicrographs, illustrate the microscopic structure of the cellulose fibre. The outstanding visible characteristic of natural cellulose revealed microscopically is its fibrillate structure. Using optical means, fibrils of a few 1000 A. are seen, but with electron microscopy much finer fibrils a few 100 A. thick can be detected. Broadly speaking, the evidence shows that the fibrils correspond to the highly ordered parts of natural cellulose, and that hydrolytic attack occurs more readily in the less ordered interfibrillar regions. Certain degradative treatments also cause transverse splitting of the fibrils into rod-like structures. There are 38 references to the literature. P. C.

Relative Efficiency of "Saturant" Bitumen as a Textile Rotproofing Agent. W. G. Atkins, S. R. Sen Gupta, and W. G. Macmillan. *J.S.C.I.*, **69**, 61–64 (Feb. 1950).

Laboratory tests have indicated that pretreatment of jute with cuprammonium followed by saturation with bitumen, or a single treatment with a mixture of bitumen and cresylic acid, provides better protection against rotting than treatment with bitumen alone. The former process is the more effective. A new rot-testing procedure is described, involving partial immersion of yarns under constant load in an aqueous extract of enriched soil until breakage occurs. W. K. R.

Protection of Mechanical Cloth with Phenyl Mercurials. P. P. Hopf and E. Race. *Ind. Eng. Chem.*, **41**, 820–827 (April 1949).

Phenylmercuric 2:2′-dinaphthylmethane-3:3′-disulphonate is an excellent rot- and mildew-proofing agent which is fast to leaching and does not cause skin irritation. C. O. C.

Laundry Resistant Anti-mildew Treatment. S. Lee. *Amer. Dyestuff Rep.*, **39**, 145–151, 156 (6th March 1950).

A mildew- and rot-resistant finish on both vegetable and animal fibres depends upon a resin-bonded, water-insoluble fungicide such as copper 8-quinolinate. After repeated laundering, dry-cleaning, and exposure to ultra-violet radiation the resistance of the treated is considerably superior to that of the untreated material. H. K.

Preparation and Properties of Cellulose Phosphates. J. D. Reid and L. W. Mazzeno. *Ind. Eng. Chem.*, **41**, 2828–2831 (Dec. 1949).

In an attempt to produce a flameproof finish which is also "glowproof", various ways of phosphorylating cotton have been investigated, and the use of phosphorus oxychloride and pyridine appeared to be the most promising. Cotton phosphorylated by these agents is flame- and glow-proof but loses so much in tensile strength as to be worthless. Use of the urea–phosphoric acid method of phosphorylation avoids much of this degradation. Incorporation of cellulose phosphates into flameproofing compositions reduces the afterglow, but too much is needed to achieve complete extinction of afterglow. Data are given on the effect of changes in time, temperature, and molar ratio on the phosphorylation of cellulose, hydroxyethyl cellulose, ethyl cellulose, and cellulose acetate. C. O. C.

Composition of Two Types of Cellulose Phosphates. J. D. Reid, L. W. Mazzeno, and E. M. Buras. *Ind. Eng. Chem.*, **41**, 2831–2834 (Dec. 1949).

The combined phosphorus in cellulose phosphate prepared by treating cellulose with the normal urea–phosphoric acid flameproofing composition is probably entirely present in a monosubstituted phosphate ester. There is no evidence of formation of other, more highly substituted products, as assumed by Coppick and Hall (*Flameproofing Textile Fabrics*, A.C.S. Monograph 104 (New York 1947), pp. 182–183). The structure of cellulose phosphate prepared by treating cellulose with a phosphorus oxychloride–pyridine mixture is similar, except that in a typical sample approx. 23% of the phosphorus can be accounted for as a disubstituted phosphate ester. The chlorine also present in this product is probably attached directly to carbons of the glucose unit. Nitrogen is also present, presumably from the pyridine. C. O. C.

Stabilisation of Casein Fibres by Desamination. R. F. Peterson and R. L. McDowell. *Text. Research J.*, **20**, 95–99 (Feb. 1950).

The effect of desamination on casein fibres has been studied, and it is shown that this process increases the wet strength of the fibre and its stability to boiling, probably by the presence of new linkages. The modified fibre, in contradistinction to the unmodified, has a yield point in its wet stress–strain curve. The new linkages are thought to be diazo* bonds. Additional stability is obtained by treating the desaminated fibre with acid formaldehyde solution and baking, although the underlying chemical reactions have not yet been demonstrated. Dye uptake of both acid and basic dyes is reduced by the combined treatment. P. C.

* Probably *azo* is meant.

PATENTS

Reducing the Felting Power of Wool and Increasing its Resistance to Abrasion. Wolsey Ltd. and P. Alexander. *B.P.* 613,267.

This specification has been amended, but the change made does not affect the abstract previously published J.S.D.C., **65**, 259 (1949)). C. O. C.

Coating Threads. C. Luria. *B.P.* 634,780.

Textile threads are coated by passing in contact with an adsorbent material impregnated with viscous material, e.g. drying or non-drying oils, soaps, resins, gums, glues, etc., which is solid or viscous at normal temperatures, but fluid at the temperature of application. J. W. B.

Coating Process. Sylvania Industrial Corpn. *B.P.* 635,344.

On a backing sheet, e.g. paper, are applied from toluene solution e.g. a phenol–formaldehyde resin (12 parts by wt.), a soft alkyd resin plasticiser (2), and a phthalic acid catalyst (0·05), which is cured to a non-thermoplastic state. A thermoplastic film is applied thereon from acetone–butyl alcohol soln., e.g. polyvinyl butyral (50), phenol–formaldehyde resin (10), and dibutyl phthalate (2). After applying to e.g. a nylon cloth the backing sheet and non-thermoplastic component are stripped away cleanly, leaving the thermoplastic film, which is then cured to a hard impervious coating.

B.P. 635,345.

The backing sheet is deformable and comprises a flexible self-supporting film of natural or synthetic resin of softening point > than the tacking point of the thermoplastic coating. J. W. B.

Stratified Polyvinyl Chloride Films. C. C. Johnson and Du Pont. *U.S.P.* 2,491,923.

Stratified polyvinyl chloride resin films or coatings, which contain in the substratum a plasticiser, e.g. polypropylene glycol sebacate, which will not migrate into the surface stratum of unplasticised polyvinyl chloride, are resistant to staining by coloured cosmetics, foodstuffs,

etc., and are innocuous to the lacquer-type finishes and printing inks used by bookbinders. C. O. C.

Organic Compounds of Titanium—Tetraalkyl Orthotitanates, New Waterproofing Agents. R. J. Speer and D. R. Carmody. (III, p. 383.)

Fungicidal Activity of Bisphenols. P. B. Marsh, M. L. Butler, and B. S. Clark. (III, p. 383.)

Polyvinylacetal Adhesives. S. Zweig and Milprint Inc. (III, p. 384.)

Interaction of Cellulose with Alkaline Solutions of Metal Hydroxides. [Determination of Cobalt.] A. Pakshver, M. Arkhipov, and B. Geller. (VI, p. 389.)

Silvering Organic Surfaces. Kodak Ltd., K-H. Sun, and L. E. Martinson. (XIII, p. 394.)

Use of Iodine Absorption in Investigations on Mercerising. K. Schwertassek. (XIV, p. 396.)

XI— PAPER AND OTHER CELLULOSIC PRODUCTS

Oxidative Stability of Cellulose Derivatives—Heat Stability of Ethylcellulose. L. F. McBurney. *Ind. Eng. Chem.*, **41**, 1251–1256 (June 1949).

Ultra-violet Light Stability of Ethylcellulose. E. F. Evans and L. F. McBurney. *Ind. Eng. Chem.*, **41**, 1256–1260 (June 1949).

PATENTS

Cellulose Ethers. Hercules Powder Co., R. W. Ivett, and W. W. Koch. *B.P.* 634,808.

Thermoplastic cellulose ethers are stabilised by incorporating 0·5–5·0% of di*iso*butylphenol, with or without 0·005–0·5% of SO_2 as such or in the form of a sulphur-releasing compound, e.g. butadiene sulphone. J. W. B.

Paper of Improved Stability to Storage and Heating. J. Studeny, C. G. Landes, and American Cyanamid Co. *U.S.P.* 2,492,821.

Incorporation of 0·3–10·0% by weight of an ammonium or alkali-metal salt of dicyanimide prevents loss in tensile strength and in tear and fold resistance when the treated paper is aged and/or heated. The colour and sizing properties of the paper are unaffected.

U.S.P. 2,492,822.

Ammonium and alkali-metal salts of dicyanoguanidine are similarly used. C. O. C.

Decorative Protective Coating Composition for Paper or other Flexible Material. C. G. Murphy, J. P. Sermattei, and Du Pont. *U.S.P.* 2,492,760.

A composition imparting high gloss comprises 75–95% of a hard aromatic-hydrocarbon-soluble resin, m.p. > 100°c., and 5–25% of a compatible copolymer of 1–10 mol. of ethylene and 1 mol. of vinyl acetate. C. O. C.

Polyvinylacetal Adhesives. S. Zweig and Milprint Inc. (III, p. 384.)

Cellulose Esters of a Stabilised Rosin Carbamic Acid. D. S. Breslow and Hercules Powder Co. (XIII, p. 394.)

XII— LEATHER; FURS; OTHER PROTEIN MATERIALS

Analysis of Organic Tannin Systems by means of Exchange Resins. R. Bosse. *Colloquiumsber. Inst. Gerbereichem. Tech. Hochschule Darmstadt*, (5), 47–59 (1949): *Chem. Abs.*, **44**, 2267 (10th March 1950).

Review of work on determination of acids and salts and their effect on the character of the leather. New data are given for acid and salt contents of four replacement syntans, determined by the ion-exchange method. Values obtained, especially for salts, are higher than for most natural tannins. For evaluating replacement syntans, determination of total acid and salt contents must be supplemented by methods for differentiating acids of different degrees of dissociation. C. O. C.

Differences and Parallelisms in Synthetic Replacement Tannins and Natural Tannins. G. Otto. *Colloquiumsber. Inst. Gerbereichem. Tech. Hochschule Darmstadt*, (5), 34–46 (1949): *Chem. Abs.*, **44**, 2267 (10th March 1950).

Natural (I) and replacement (II) tannins are similar in respect to— (1) Structure— Both contain several benzene rings with many weakly acidic groups. This appears to be a sufficient criterion of a tanning agent. (2) Acidity— Potentiometric titrations in dil. soln. give p*K* values (corrected for non-tannins) of 8·0–9·8. In I the acid strength is enhanced by the mutual influence of several phenolic OH groups attached to one benzene ring; in II the acidity of the less numerous OH groups is enhanced by other polar groups, e.g. neutralised sulpho groups. (3) Precipitation by Grassmann's reagent — Turbidity increases with astringency for both I and II. (4) Presence of molecular species of differing degrees of aggregation and astringency. (5) Existence of a variety of types suitable for making different types of leather when used alone or in appropriate mixtures. II differs from I in containing fewer phenolic groups, in containing neutralised sulpho groups, in not giving a colour with Fe^{3+} (except II made from dihydroxybenzene derivatives), and especially in the nature of the non-tannins. In II the non-tannins are chiefly inorganic salts and organic acids deliberately added. II contains no sugars, and does not produce acid by fermentation. II does not deteriorate on aging as does I through oxidation, fermentation, and resinification. II dissolves encrusted I from tan vat walls. The vats may need a protective lining. The analytical fixed tannin content of leather made from I increases on long storage at the expense of water-soluble matter. With II this increase is shown only by dihydroxybenzene derivatives. C. O. C.

Constitution and Tanning Action of Phenolic Syntans. R. Biedermann. *Colloquiumsber. Inst. Gerbereichem. Tech. Hochschule Darmstadt*, (5), 25–33 (1949): *Chem. Abs.*, **44**, 2268 (10th March 1950).

Tanning power decreases with increasing degree of sulphonation, and increases with degree of condensation to a maximum and then declines with overcondensation. The rôle of the phenolic OH group is minor in syntans of the Neradol type (formaldehyde-condensed phenol-sulphonic acid), as etherification hardly affects their tanning power, but is more marked in phenolnovolak syntans (sulphonated phenol–formaldehyde condensates). Phenolic OH plays an increasingly important rôle when its acidity is raised by constitutional changes, e.g. in syntans from sulphonyldiphenol (Irgatan IV). Differences in tannin contents of syntans, and in relationships between concentration and apparent ratio of tannin to total solids determined with hide powder, are frequently at variance with actual tanning power determined with whole skin. C. O. C.

Quinone Tanning in the Animal Kingdom. H. Burton and J. L. Stoves. *Nature*, **165**, 569–570 (8th April 1950).

When dilute aqueous solutions of 2:4:5-trihydroxytoluene or hydroxyquinol are applied to human skin, a brown–black stain develops in 8–24 hr. It is postulated that the trihydroxy compounds, fuctioning as reducing agents, convert some disulphide bonds of the keratinous protein into mercapto groups, which then react with the hydroxyquinone produced to give a thio compound capable of undergoing oxidation to the thio quinone. Iron present in the skin or blood is co-ordinated into the final structure to give the brown–black complex. Similarly, wool can be dyed brown by aqueous solutions of these two trihydroxy compounds, and simultaneous treatment with ferrous, cupric, or cobalt salts causes a marked darkening of the colour, which is almost black when ferrous iron is used. A. S. F.

Aqueous Zein Dispersions. C. W. Ofelt and C. D. Evans. *Ind. Eng. Chem.*, **41**, 830–833 (April 1949).

Zein is dispersible in strong alkali-metal hydroxides only within the narrow pH range 11·3–12·7. Quaternary ammonium hydroxides are also dispersing agents, but somewhat inferior to the alkali-metal hydroxides. Zein is not dispersible in ammonium hydroxide or in calcium hydroxide solutions. The amount of alkali required to disperse zein is low; based on the weight of zein, 1·4% (minimum) to 6·4% (maximum) of sodium hydroxide is required for the preparation of a 10% zein dispersion. The dispersibility of zein is attributed to the formation of the alkali-metal salts of the phenolic hydroxyl groups of tyrosine. Zein is dispersible also in strong acids (12N-HCl). The pH–dispersion curves, viscosity curves, and stability data are presented for aqueous alkali–zein dispersions. M. E. W.

XIII—RUBBER; RESINS; PLASTICS

Ignition and Burning Characteristics of Polyester, Phenolic, and Melamine Fibrous Glass Laminates. H. J. Stark. *ASTM Bull.*, 55–58 (Dec. 1949).

PATENTS

Ornamented Rubber Sheeting. S. C. Nielsen. *B.P.* 635,091.

Holes are made in one or more layers of uncured rubber, which are superimposed on similar sheets without holes and of different colour; vulcanisation under pressure causes the lower sheet to fill the holes, thus producing an imitation inlaid pattern on the upper surface. J. W. B.

Chlorination of Rubber Latex. Rubber Stichting. *B.P.* 634,241.

Rubber latex is made stable to acids by adding a non-ionic or cationic surface-active agent, adjusted to an acidity >3N. by adding an acid, e.g. HCl, and chlorinated. The product is a stable latex of chlorinated rubber substantially free from combined oxygen. E. C.

Cellulose Esters of a Stabilised Rosin Carbamic Acid. D. S. Breslow and Hercules Powder Co. *U.S.P.* 2,492,928.

The products obtained by treating cellulose or any of its derivatives containing unreacted hydroxyl groups with the *iso*cyanate of a stabilised rosin acid have the desirable properties of cellulose coupled with those of the stabilised rosin nucleus. In addition to their resinous properties they are more soluble in organic solvents than the hitherto known cellulose carbamates. They have outstanding resistance to hydrolysis, especially acid hydrolysis. Those prepared from partly substituted cellulose ethers are compatible with other film-formers and resins. C. O. C.

Plasticisers for Vinyl Resins. Carbide & Carbon Chemicals Corpn., F. Johnston, and W. H. Hensley. *B.P.* 635,011.

Plasticisers for vinyl resins are diester-amides of formula $R^1{\cdot}CO{\cdot}N(C_2H_3R^2{\cdot}O{\cdot}CO{\cdot}R^1)_2$ (R^1 = Alk of 2–8 C; R^2 = H or CH_3), e.g. 2:2′-(2″-ethylhexanamido)diethyl di-(2-ethylhexanoate). W. G. C.

Heat Stabilisation of Vinylidene Chloride Resins. Distillers Co. Ltd.; C. A. Brighton, and D. Faulkner. *B.P.* 634,762.

Resins containing >25% vinylidene chloride are stabilised to heat degradation by incorporating 2–10% of a neutral functionally aliphatic ester of an aliphatic polyhydroxy acid in which any free hydroxyl group occurs only on the acid residue, e.g. dibutyl tartrate. W. G. C.

Transparent Polyamides. Du Pont. *B.P.* 634,235.

The transparency of polyamides is improved by incorporating 0·5–10% by weight of a compound of formula $R^1{\cdot}CO{\cdot}X{\cdot}R^2{\cdot}SO_3M$ (R^1 = a hydrocarbon chain containing 11–19 C, R^2 = a bivalent hydrocarbon radical of 1–6 C, M = Na or K, and X = O or NAlk), e.g. sodium 2-oleoyloxyethanesulphonate. W. G. C.

Polyamide Compositions. R. H. Schlattman and Monsanto Chemical Co. *U.S.P.* 2,491,934.

Polyamide compositions of decreased water permeability are prepared by incorporating hydroxy-substituted diphenyl sulphones, e.g. 4:4′-dihydroxydiphenyl sulphone. *U.S.P.* 2,491,935.

Polyamide compositions of increased resistances to the effects of changes in humidity are obtained by incorporating *o*-sulphobenzimide. *U.S.P.* 2,491,936.

Polyamide compositions of increased flexibility at low temperatures are obtained by using a mixture of *N*-ethyl-*o*- and -*p*-toluenesulphonamides and *o*-sulphobenzimide as the plasticiser. C. O. C.

Moulding Poly-*N*-vinylcarbazole. General Aniline & Film Corpn., W. F. Busse, and J. M. Lambert. *B.P.* 634,077.

Products of good electrical and mechanical properties are obtained by moulding a mixture of comminuted oriented fibres of polyvinylcarbazole and 15–35% of an *N*-vinylcarbazole of lower softening point, at slightly above the lower softening point. W. G. C.

Silvering Organic Surfaces. Kodak Ltd., K-H. Sun, and L. E. Martinson. *B.P.* 635,101.

Organic surfaces, e.g. synthetic plastics or textiles, or ceramics, e.g. Fiberglass or silicone fibres, are rendered capable of being coated with silver, if they are treated with a compound of formula R_nMHal_{4-n} (R = CH_3, C_2H_5, or C_6H_5; M = Si, Ti, Sn, or Ge; n = 1, 2, or 3), e.g. dimethylsilicon dichloride.

B.P. 635,102.

A compound of formula $MHal_4$ (M = Si, Sn, Ti, or Ge) is used. C. O. C.

Exfoliating and Bleaching Vermiculite. J. B. Baines. *U.S.P.* 2,492,208.

Vermiculite is exfoliated and bleached by treatment in nitric acid of sp. gr. 1·02–1·42 to which has been added 1–20% of phosphoric acid. The product is translucent to transparent, is readily dyed, and is useful for incorporation into plastics to give a beautiful sparkling depth of colour. C. O. C.

Polyvinyl Acetate Emulsions. Shawinigan Resins Corpn. (III, p. 383.)

Modified Furfuryl Alcohol Resins. Quaker Oats Co. (III, p. 384.)

Polyamides. Wingfoot Corpn. (VI, p. 390.)

Hydrolysed Ethylene Interpolymers. I.C.I. Ltd. (VI, p. 390.)

Plasticisers for Polyvinyl Chloride. Compagnie Française de Raffinage. (VI, p. 390.)

Synthetic Preparations from Starch. D. Horsak. (VI, p. 390.)

XIV—ANALYSIS; TESTING; APPARATUS

Chromatography of Proteins. J. I. M. Jones and S. E. Michael. *Nature*, **165**, 685 (29th April 1950).

A simple method of location of proteins on a paper chromatogram or a cellulose column is described, based on the affinity of acid dyes for protein fibres and not for cellulose. The developed chromatogram is treated with a 0·05% solution of a suitable dye, e.g. Solway Purple, containing 0·5% sulphuric acid in a photographic developing dish at 50–90° C. The proteins show up as violet patches on the chromatogram. This dyeing property has been used for a study of the movement of proteins along the chromatogram using different liquids. H. H. H.

Characterisation of Some Commercial Soaps by X-Ray Diffraction. G. S. Hattiangdi. *Bur. Stand. J. Res.*, **42**, 331–341 (April 1949).

Characterisation of Alkali Soaps by Electron Microscopy. G. S. Hattiangdi and M. Swerdlow. *Bur. Stand. J. Res.*, **42**, 343–360 (April 1949).

The morphological differences between several closely related alkali soaps have been determined by the techniques of electron microscopy. The crystalline alkali soaps consist of an interlocked mesh of bundled fibres, whereas the liquid-crystalline soaps exhibit a flagellar and/or featureless phase. The micellar groupings for the individual soaps are unique, and a scheme based upon the electron micrographs is suggested for their characterisation. The structures of Li, Na, and K palmitates are closely related. The laurate, palmitate, and stearate of Na also exhibit homologous structures. The results of these morphological investigations offer a rapid and accurate means of identification, and have been successfully applied to the problem of characterising commercial soaps of unknown composition. M. E. W.

Evaluation of Detergents for Textile Cleaning. W. P. Utermohlen and M. E. Ryan. *Ind. Eng. Chem.*, **41**, 2881–2887 (Dec. 1949).

Present methods of evaluating detergent action on textiles using reflectance data give only relative soil-removal values when applied to washed cloths soiled with a black iron oxide. Soil-removal values calculated by the linear method from reflectance data do not agree with either the values calculated by using the Kubelka–Munk equation from reflectance data (when applied to crushed cloth soiled with carbon black or iron oxide) or the absolute values obtained by analysis for iron where iron oxide was the soil. Furthermore, the Kubelka–Munk soil-removal

values agreed with the analysis values for only some of the detergent systems studied. As reflectance measurements often fail to portray the true pigment soil content in washed cloth soiled with black iron oxide, it would appear that the common practice of using such reflectance data to estimate the true pigment soil content, when using pigments such as carbon black, should be critically re-examined. Detergency calculation based on chemical analysis for the pigment soil appears to be worth consideration, although reflectance measurements may be preferable if surface appearance alone can be accepted as the criterion of the extent of cleaning. All laboratory estimates of detergent value should be considered only as screening tests to guide the way for works tests, upon which the final selection of a detergent system should be based. C. O. C.

Evaluation of Dispersing Agents [and of the Dispersibility of Acetate Rayon Dyes]. A.A.T.C.C. New York Sectional Advisory Research Committee. *Amer. Dyestuff Rep.*, **38**, P 947 (26th Dec. 1949).

The following tentative test method has been suggested—

APPARATUS—Buechner funnel, with inside plate 9 cm. wide; 500-ml. suction flask; suction to give 150 mm. mercury; 250-ml. beaker; 100-ml. graduated cylinder; 2-ml. pipette.

MATERIALS—Desized and bleached 80 × 80 cotton print cloth, cut into filter discs of 9 cm. diameter.

TEST SAMPLE—Normal commercial product; if experimental product, allow for any difference in strength from commercial product.

PROCEDURE—1·0 g. Commercial dye, or its equivalent, is pasted with 2 ml. water. A disc of filter cloth is placed in the Buechner funnel, suction applied, and 150 ml. water at 170°F. poured through so as to warm the funnel and seat the cloth. 100 ml. Water at 160°F. is added to the paste, and the mixture stirred steadily with a glass rod for 30 sec. The mixture is immediately filtered, and the cloth removed and air-dried. Other temperatures can be used to study the effect of temperature on dispersibility. To test the stability of the suspension, the dispersed dye is stirred for 30 sec., and then allowed to stand before filtration.

EVALUATION—The residue left on the cloth is observed visually. If the amount is slight, covering only the funnel holes, dispersibility is graded "excellent", if the cloth is light-coloured "good", and if the cloth is heavily covered "poor". Attempts to correlate dispersibility as indicated by the above method with speckiness in dyeing and padding failed. Dyes which had poor dispersibility according to the above test frequently dyed satisfactorily. C. O. C.

Methods of Determination of the Silica and Halogen Contents of Some Organic Compounds of Silicon. D. Ridge and M. Todd. *J.S.C.I.*, **69**, 49–51 (Feb. 1950).

Methods are described for the determination of silica and halogen in organic silicon compounds, including volatile and moisture-sensitive substances. W. K. R.

Quinone Chlorimines as Colour Reagents for Phenols. R. Castle. *Chem. and Ind.*, **16**, 313 (22nd April 1950).

Aromatic amines are found to react with 2:6-dichloroquinonechloroimine, which also gives rise to highly coloured products with various naturally occurring compounds such as *a*-biotin. It is suggested, therefore, that the use of quinonechloroimines as specific colour reagents for phenols is unsatisfactory (cf. Gibbs, *J. Biol. Chem.*, **72**, 649 (1927) and Bradley, *Ind. Eng. Chem. Anal. Ed.*, **3**, 304 (1931)), owing to their lack of specificity, and that other reagents of an electrophilic character, e.g. 4-aminoantipyrin (cf. Martin, *Anal. Chem.*, **21**, 1419 (1949)), alleged to be specific for phenols, are not so. H. H. H.

Some Colour Reactions of Phloroglucinol. D. Ismay. *J.S.C.I.*, **69**, 58–59 (Feb. 1950).

Phloroglucinol in the presence of conc. HCl gives a red colour with certain aldehydes and with the oxidation products of quinols and *p*-quinones. Only the aldehydes, however, give a red colour with substituted phloroglucinols (e.g. methyl phloroglucinol or phloroglucinol di- or trimethyl ether). No colour is produced with pure allyl compounds, the red colour usually obtained being due to the presence of aldehyde impurities. W. K. R.

Identification of Azoxy Compounds. R. Gaudry and K. F. Keirstead. *Canadian J. Res.*, **27 B**, 897–901 (Dec. 1949).

The Wallach rearrangement, in which an azoxy compound is converted into a hydroxyazo compound by treatment with excess of conc. H_2SO_4, is suggested as a generic test for the former. An azoxy compound so treated becomes bright red in colour and soluble in the acid; it is precipitated on pouring into water, but is soluble in dil. alkaline solution. Individual azoxy compounds may be identified by preparation of (*a*) the hydrazo compound by reduction with zinc dust, and (*b*) the azo compound by air oxidation of an alcoholic solution of (*a*). W. K. R.

Determination of Juglone in Juglandaceæ. G. Petrosini and T. Eschena. *Boll. Soc. ital. Biol. sper.*, **24**, 846, 847 (1948): *Chem. Abs.*, **44**, 2174 (10th March 1950).

Powder 1–5 g. plant material with sand, add 5 c.c. sat. $SnCl_2$, extract with water, fill up to 100 c.c., and centrifuge. Precipitate the Sn in 50 c.c. clear centrifugate by H_2S, filter, acidify with HCl, and remove excess H_2S by CO_2 or N_2. Add to an aliquot of the filtrate 3 c.c. NH_4OH (sp. gr. 0·90) and fill up to 100 c.c. Measure in the electrophotometer within 20 min. Beer's law is followed up to 7 p.p.m. juglone. C. O. C.

Application of the Differential Dyeing Test for Fibre Maturity to the Processing of Cotton. A.A.T.C.C. Southeastern Section. *Amer. Dyestuff Rep.*, **39**, P 74–P 77, P 90 (6th Feb. 1950).

An immaturity test for cotton fibres is based upon the differential absorption by the fibre of a red and a green dye, both being applied in the same dyebath. The technique has been utilised in the control of the blending of raw cottons, excessive neppiness, and tippiness. H. K.

Moisture Determination by Electrical Methods. H. Mahlo. *Textil-Praxis*, **5**, 73–76 (Jan.), 176–180 (March 1950).

A discussion of electrical methods of moisture determination of textiles and their application to different branches of the textile industry, including weaving, sizing, and finishing. B. K.

Methods of Testing for Moisture in Wool. G. C. LeCompte and H. H. Lipp. *Amer. Dyestuff Rep.*, **38**, 484, 512 (27th June 1949).

Of the five methods tested—(*a*) vacuum over P_2O_5, (*b*) conditioning oven at 110°c., (*c*) U.S. Dept. of Agriculture suction drier, (*d*) forced-draught drier, and (*e*) toluene distillation—the last gave the most accurate results. Methods (*b*), (*c*), and (*d*) gave incomplete results for moisture, apparently because present-day ovens operate in atmospheres containing appreciable amounts of moisture; they might yield accurate results if means were developed for a continuous supply of an anhydrous atmosphere. C. O. C.

Felt Tests and Specifications and their Interpretation. R. R. Stevens. *ASTM Bull.*, 48–49 (Feb. 1950).

An explanation is given of why certain tests are included in felt specifications. The possibilities of using fluorescent dyes and materials activated by ultra-violet radiation in the testing of felt are indicated. H. K.

Fugitive Tint on Natural Silk. J. Pinte and Mme. Pierret. *Bull. Inst. Textile France*, (8), 33–40 (1948): *J. Textile Inst.*, **40**, A 20 (Jan. 1950).

A photometric study has been made to determine the minimum concentration of solutions of fugitive tints which may be employed on natural silk to differentiate yarns of different characteristics used in the production of a fabric, as well as the limit concentration which must not be exceeded to obtain a completely colourless yarn after scouring. The results for eight recommended fugitive tints are tabulated, and show that with correct choice of concentration and experimental conditions all the tints used are completely removed by the normal scouring process. M. E. W.

Evaluation of Enzymatic Desizing Agents. E. Schubert. *Amer. Dyestuff Rep.*, **39**, 181–189, 202 (20th March 1950).

Translated from *Textil-Rund.*, **3**, 295–304 (Sept.), 335–341 (Oct. 1948): J.S.D.C., **65**, 425 (Aug. 1949).

Recent Developments in the Measurement of Detergency. G. Marroc and J. P. Sisley. *Teintex*, **15**, 125–139 (March 1950).

A review of methods of assessing detergency, with 54 references to the literature. Two new pieces of apparatus for detergency determinations are described, viz. the Terg-o-Tometer (General Aniline) and the Lavomatic (H. Rua & Co.), the latter being the first-named author's modification of the Terg-o-Tometer. Soiled patterns are agitated by mechanical stirrers, and the detergent effect is assessed by reflectance measurements. The relationships between detergency and temp., and between redeposition of soil and temp., are given graphically. B. K.

Use of Iodine Absorption in Investigations on Mercerising. K. Schwertassek. *Melliand Textilber.*, **31**, 188–192 (March 1950).

The iodine absorption method for determining degree of mercerisation is reviewed, and the theory of the method considered. It is concluded that the iodine is absorbed only in the amorphous region of the fibre. The extent of absorption thus constitutes a measure of degree of crystallisation, and enables changes in the fine structure of the fibre during the processes of rinsing and drying to be followed. F. A.

Report of Committee for Nomenclature and Classification. A.A.T.C.C. *Amer. Dyestuff Rep.*, **38**, P 489 (27th June 1949).

The following has been adopted as the A.A.T.C.C. official nomenclature for fastness and other ratings—

NUMBER OF DEGREES OF FASTNESS OF DYEING— There shall be eight degrees of fastness for light, with class 8 the best quality and class 1 the poorest; five degrees of fastness for most other properties, with class 5 the best in quality and class 1 the poorest; and three degrees of fastness for a few properties, where five steps seem excessive, with class 5 the best in quality, class 3 medium in quality, and class 1 the poorest in quality.

TERMS FOR FASTNESS TO LIGHT— Classes 8–1 are termed *maximum*, *excellent*, *very good*, *good*, *fairly good*, *fair*, *poor*, and *very poor* respectively.

FASTNESS TERMS FOR MOST OTHER PROPERTIES— Classes 5–1 are termed *excellent*, *very good*, *good*, *fair*, and *poor* respectively.

DEGREE OF STAINING OF EFFECT THREADS— Classes 5–1 are referred to as—*virtually unstained*, *slightly*, *considerably*, and *heavily stained*, and *dyed* respectively.

EFFECT OF METALS ON DYEINGS— Classes 5, 3, and 1 are *virtually unchanged*, *slightly changed*, and *considerably changed* respectively.

DISCHARGEABILITY OF DYESTUFFS— The classes are 5— Discharges white in all depths of shade. 4— Discharges white in light and medium shades; slightly tinted in deep shades, or develops a slight tint in storage. 3— Discharges sufficiently for printed coloured effects but not for whites. 2— Discharges poorly; not suitable for printed coloured or white effects. 1— Does not discharge (suitable for use in printing colour discharges). M. E. W.

Note on Various Methods for Determining Extent of Co-ordination to Trivalent Chromium of Organic Acid Anions. S. G. Shuttleworth. *J. Soc. Leather Trades Chem.*, **34**, 3–6 (Jan. 1950).

The ionic sulphate method is not recommended for determining penetration of organic anions into chrome complexes, since the liberated sulphate is the result of three equilibria, viz. rapid hydrolysis of complex-bound sulphate, its replacement by organic anion, and readjustment of ionic and non-ionic sulphate to a new equilibrium. The conductimetric method may fail to distinguish between free weak acid and the complex, although this weakness does not detract seriously from its main usefulness in following the ionic mobility changes and the reaction of complexes with acid and alkali. The solvent extraction method is limited to estimation of monofunctional molecules such as monobasic acids. The deficiencies of the conductimetric method also apply to potentiometric titration, while the spectrophotometric method is at present limited to organic acid groups, such as oxalates, which form end-products of known constitution. H. H. H.

Light Absorption and Fastness of Dyes. S. Sakurai. *Rept. Japan. Assocn. Advancement Sci.*, **16**, 547, 548 (1942): *Chem. Abs.*, **44**, 2753 (25th March 1950).

Dyes whose light absorption curves dip deeply fade readily in light, whereas dyes having shallow absorption curves are fast to light. Thus the absorption curves can be used as a measure of fastness of dyes to light. C. O. C.

Photodegradation of Dyes on Matt Acetate. Influence of Bleaching on Degradation. J. Pinte and Mlle. Goujet. *Bull. Inst. Textile France*, (5), 11–24 (1948): *J. Textile Inst.*, **40**, A 20 (Jan. 1950).

The extent of degradation under the influence of sunlight suffered by dyed samples of dull and of lustrous acetate rayons is found to be greater for the dull samples than for the lustrous ones. The dulling agents thus seem to play the part of catalysts in the degradation reaction. For dulled acetate samples, bleached before dyeing according to different classical procedures, it was found that degradation was a maximum for hypochlorite bleachings carried out at pH 7 and 4. Experimental results are presented in graphs and tables. M. E. W.

Photochemistry of Rutile. W. A. Weyl and T. Förland. (III, p. 383.)

Bromination of Cresol. N. Ray. (IV, p. 384.)

Interaction of Cellulose with Alkaline Solutions of Metal Hydroxides. [Determination of Cobalt.] A. Pakshver, M. Arkhipov, and B. Geller. (VI, p. 389.)

XV— MISCELLANEOUS

Toxicity of Solvents. A. J. Amor. *Paint*, **20**, 53–58 (Feb.), 89–93 (March 1950).

Notes and tables on the toxicity of individual members of all classes of industrial solvents are given. C. O. C.

The Sulphathiazole [Patent] Case. S. I. Levy. *Chem. and Ind.*, 246–248 (1st April 1950).

This paper discusses the status of patents for new substances, and is based on the recent revocation of a patent owned jointly by May & Baker Ltd. and Ciba Ltd., which claimed the manufacture of benzenesulphonamidothiazole derivatives by known methods. This patent was held to be bad for want of subject matter, want of utility, and false suggestion. It was further held that amendment was not allowable. It follows from the Report of the Appellate Committee of the House of Lords on 9th Feb. 1950 that the Courts will uphold patents for new substances made by known methods, provided that the new substances are useful, and that the specification complies with the requirements of the patent law. The judgments are therefore encouraging for the whole chemical industry, and especially for the therapeutics industry, and are valuable as laying down on the highest authority the conditions which must be fulfilled in order that patents granted for chemical processes and new substances may be valid. The particular questions now dealt with are— *What constitutes invention*, *What is not invention*, *The question of amendment*, and *Present law as to new substances*. It is shown that the preparation of a substance which has valuable properties may therefore constitute invention, provided that the substance is new, and that it could not have been foreseen that when made it would be found to possess those particular valuable properties. The discovery of valuable therapeutic properties in a known substance cannot form the subject of a patent, but such a discovery in respect of a new substance may constitute invention. The new provisions as to amendment are intended to provide a means whereby a patentee who has made an invention, and has fairly described it in his specification, may avoid the loss of his patent, even though by inadvertence or by taking too wide a view he has claimed something more than the invention he has made. However, claims wider than those necessary to protect the invention made will be looked at closely; if the Court concludes that a claim has been framed deliberately to mark out too wide a territory, with the object of preventing others from working in the field, its discretion may well be exercised to refuse amendments which would otherwise be allowable. This classification of the law as to the degree of invention required in the field of chemotherapeutics will be very welcome to the industry, viz. that, where the properties of a new substance cannot fairly be estimated in advance, each new substance found to have valuable properties constitutes a separate invention. The new Act no longer contains a provision forbidding claims to a new substance *per se* without limitation to the method of manufacture. H. H. H.